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TO PROMOTE THE STUDY OF ELECTROCHEMISTRY ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS

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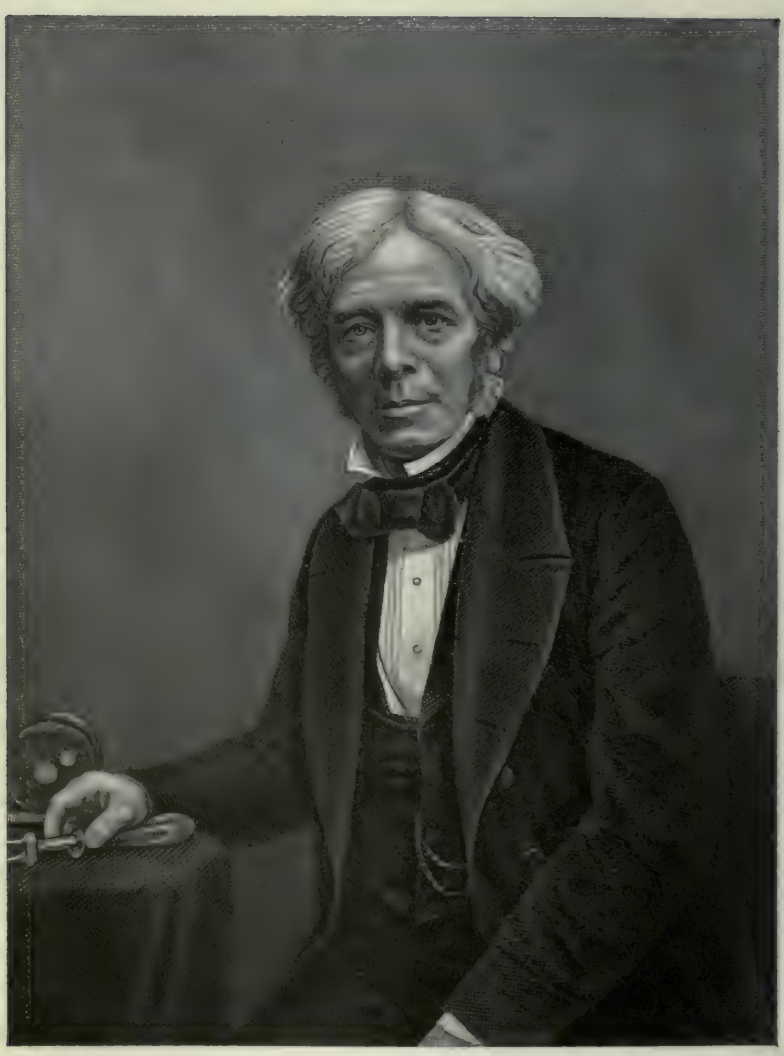

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VOL. X. AUGUST, 1914. PART 1.

ADVANCES IN THE METALLURGY OF IRON AND STEEL.

BY SIR ROBERT HADFIELD, F.R.S.

(A PRESIDENTIAL ADDRESS *delivered to the Faraday Society on Thursday, June* 11, 1914, DR. R. T. GLAZEBROOK, C.B., F.R.S., PAST-PRESIDENT, *in the Chair.*)

I esteem it a great honour to be asked to take this presidential chair, filled as it has been by such men as the late Sir Joseph Swan, our first President, and above all by Lord Kelvin, whose personal kindness to myself in times gone by I can never forget. Any reluctance felt in accepting your invitation was, I assure you, due to the fact that not very robust health resulting from overwork made me chary at first of undertaking what I feared might not be possible for me to fulfil. This reluctance on my part, however, was overcome on the one part by the kind and friendly influence of our fellow Member of Council, Professor Huntington, whom I may call a brother-metallurgist—for in view of the long time we have known each other, and the kind of work in which we have each been engaged I venture to use this fraternal appellation—on the other part by the very kind offer of our indefatigable Secretary, Mr. F. S. Spiers, who promised to continue doing most of the routine work and leave but little for me.

Whilst this address is necessarily written from the standpoint of ferrous metallurgy, there is no need to apologize for bringing these views before you, seeing that Faraday himself took so much interest in the metallurgy of iron and steel.

As regards the object of our Society, its motto or text is "To promote the Study of Electrochemistry, Electrometallurgy, Chemical Physics, Metallography, and Kindred Subjects." The Society was founded in the year 1903. Our past Presidents have been the late Lord Kelvin, F.R.S., the late Sir William Henry Perkin, F.R.S., the late Sir Joseph Swan, F.R.S., Mr. J. Swinburne, F.R.S., Dr. R. T. Glazebrook, F.R.S.

Cannot our membership be enlarged? We have now a roll-call of some 200 members. Our sister Society in America, the American Electrochemical Society, has a considerably larger number—in fact, five times as many.

The name of our Society, "THE FARADAY SOCIETY," is one to conjure with, and one that we may well feel proud to own. The name has always appealed to me, because Faraday, apart from his other scientific work, paid no small attention to the particular corner of scientific research to which I

personally have devoted most of my life, the study of the numerous alloys of iron with other elements. Although Faraday was not the first in this field, yet he was certainly one of the pioneers. This is indicated and set forth in his admirable papers on alloys of steel.* The extraordinary advances which have been made throughout the world during the last generation, one might say within the last twenty years, have been largely owing to the study and introduction of new combinations of iron with other elements. Among Faraday's numerous discoveries were: Induction currents, which eventually gave us electric light and the electric motor, the law of chemical decomposition in electrolysis styled Faraday's law, diamagnetism, the action of magnets on polarized light, the liquefaction of carbonic acid gas and of protoxide of nitrogen, and many others of importance.

Early Metallurgy and Alloys of Iron and Steel.

The problem of alloys of carbon and of many different elements with the world's leading metal—*iron*—is an extraordinarily fascinating one. I use the qualificative "leading" advisedly, since without this metal the world would be plunged into uncivilized darkness, and when this metal does fail, for fail it must at some future time, it is difficult to see how the world can avoid returning to the Stone Age at a quicker pace than that at which it emerged from it. Iron is in truth the leading metal. It is constantly used and in everybody's hand and service in some shape or other and for an immense variety of purposes; yet we all recognize that it still embodies a vast amount of secrets, it still affords a wonderful field for research.

One can picture to one's self the joy of the first metallurgist, apparently Tubal Cain, when, in the early history of mankind, he discovered that a lump of red-looking, earthy material tossed by accident in his fire gave quite another material, a "metallic" product which could be made to cut. This first member of the prehistoric Iron and Steel Institute was not long in recognizing the far-reaching consequences of his accidental discovery. He, no doubt, first made weapons—a crude type of javelin presumably—from this new product, but, appalled at the rate at which the men of his period had become able to destroy one another by reason of this discovery of his, he probably endeavoured to counteract the action of the new offensive weapon he had been able to put in their hands by providing them with defensive ones, and he gave them "metallic" shields. But by that time others had entered the field and started producing both classes of weapons, making each alternately the stronger, and so matters progressed; the idea caught on, and Tubal Cain, besides being the first metallurgist, was probably also the first man to initiate the "projectile *versus* armour" conflict, a conflict which has continued ever since, is being continued to this day, and one in which my city of Sheffield, I venture to think, has acquired a world-wide renown. As regards this early history of metallurgy, I have very fully dealt with comparatively early metallurgical products, though only going back some fifteen or sixteen centuries, in my paper to the Iron and Steel Institute, "Sinhalese Iron and Steel of Ancient Origin," read in May, 1912.

Ancient Iron and the Delhi Pillar.

It may be interesting to add here that thanks to the kindness of Mr. J. H. Marshall, C.M.G., C.I.E., the Director-General of Archæology in India, since

* Faraday's Papers on the alloys of steel (Faraday and Stodart) were read on March 21, 1822, and appear in the *Philosophical Transactions* of the Royal Society for that year (p. 253); also in the *Philosophical Magazine*, vol. ix., p. 363. An interesting report of his various experiments will also be found in his work entitled *Experimental Researches in Chemistry and Physics* (1859).

PLATE I.—THE DELHI PILLAR.

my paper was written I have been able to obtain a specimen of the famous Delhi Pillar, which is about 24 feet in length and weighs 6½ tons. Plate I is a photograph of this pillar. It was found to have the following composition :

C.	Si.	S.	P.	Mn.	Fe.	Sp. G.
·080	·046	·006	·114	nil	99·720	7·81

Brinell ball hardness number 188.

This unique specimen is probably one of the finest specimens of iron-work ever produced until modern times. In other words, until less than one hundred years ago a forging of such length and weight could not have been obtained. Therefore, great credit is indeed due to the Eastern metallurgist who worked up such a specimen of the metallurgical art. As to the manner in which this was accomplished I have dealt with the problem in my paper before referred to.

Faraday's Experiments in 1822.

From Tubal Cain to Faraday is a far cry indeed. The latter, our revered master, whose name has so wisely been adopted by our Society, was one of Britain's noblest sons. In the earlier years of his activity he attacked the problem for the sake of the problem itself. His whole life was one of untiring energy, and a detailed record of his researches would fill volumes of any Institute's proceedings. He devoted a certain amount of attention to the study of metallurgy. As regards his metallurgical research work, fully described in the source to which I have previously referred, it was in 1822 he mentioned in one instance that he himself could not go to Sheffield, where he intended to have his alloys made in continuance of the experiments he and Stodart had started at the Royal Institute, but that he was carefully preparing in London the mixtures to be melted in Sheffield, placing them in separate parcels. The work was to be given to a trusty assistant, who was to go down and see the experiments put in hand and completed at Sanderson's works, this firm being still in existence to-day. In those early days there was only one way of sending the specimens from London to Sheffield—that is, by coach, a long journey, and one can picture the great scientist carefully sorting out his materials, various alloys and iron, for mixing together in order to produce the different classes of material he had in view, and carefully packing them in different parcels.

Faraday foresaw that metallurgy was destined to become one of the leading branches of science, and that in a general way it is upon progressive metallurgy that most of the advances in modern effort and progress are dependent. I say this advisedly, for what would life be to-day without the aid of the metal iron and its alloys and combinations? This was pointed out very fully in my Presidential Address to the Iron and Steel Institute in 1905. So much was I then imbued with this spirit that in that address I gave the portraits of some twenty-one early scientists, largely Swedish, to whom the world owes such a great debt of gratitude with regard to the work they did in first separating many of the various elements now used in the alloys of iron and steel. Probably in no country was more good work done than by these early scientists in Sweden.

Early Workers in Metallurgy.

It may be interesting to give a list of these early workers in scientific metallurgy ; of those against whose names an asterisk is placed I have been able to obtain portraits.

Early Workers in Scientific Metallurgy.

Aristotle (Greece), 384–322 B.C., philosopher, described the manufacture of Indian steel.

Theophrastus (Greece), 374–287 B.C., philosopher, wrote on iron ore.

Diodorus Siculus (Sicily), 60 B.C., geographer, described the smelting of Elba ore.

Plinius (Italy), 79–23 B.C., naturalist, showed that the properties of iron depend upon its treatment.

Rugerus Theophilus (Germany), monk, dealt with iron in his *Schedula diversarum Artium* (1050).

Leonardo da Vinci (Italy), 1452–1519, physicist, artist, etc., introduced blast for smelting iron.

Vanuccio Biringuccio (Italy), 1480–1539, dealt with iron in his *Pyrotechnia* (1540).

Georgius Agricola (Germany), 1490–1555, dealt with metallurgy of iron in his *De Re Metallica* (published 1556).

Lazarus Ercker (Germany), wrote on assaying (1574).

Louis de Geer (Sweden), 1587–1652, introduced the Walloon furnace.

Dud Dudley (England), 1599–1684, first smelted iron with pit coal.

Johann Rudolf Glauber (Germany), 1604–1668, chemist, discovered several metallic chlorides.

Simon Sturtevant (England), dealt in his *Metallica* with the use of coal for smelting (1612).

John Rovenzon (England), dealt in his *Metallica* (1613) with the use of coal for smelting.

*Sir John Pettus, Knight (England), 1613–1690, author of metallurgical works.

Andrew Yarranton (England), 1616–1684, introduced tinplate manufacture.

The Hon. Robert Boyle (England), 1627–1691, chemist and physicist.

*Sir Isaac Newton, Knight (England), 1643–1727, scientist.

*René Antoine Ferchault Réaumur (France), 1683–1757, physicist, wrote on cementation and decarburization.

*Emanuel von Swedenborg (Sweden), 1688–1772, engineer and theologian, wrote on iron.

G. Brandt (Sweden), 1694–1768, discovered cobalt (1733).

*Benjamin Huntsman (England), 1704–1776, manufacturer, first to melt steel.

*Benjamin Franklin (United States), 1706–1790, statesman and scientist, inventor of the Franklin stove.

Johann Andreas Cramer (Germany), 1710–1777, author, wrote on metallurgy.

Abraham Darby (England), 1711–1763, used coke for smelting.

*Sven Rinman (Sweden), 1720–1792, wrote on metallurgy of iron.

*Axel Frederic Cronstedt (Sweden), 1722–1765, mineralogist, discovered nickel (1751).

*Joseph Priestley (England), 1733–1804, chemist, discovered oxygen (1774).

*Richard Kirwan (Ireland), 1733–1812, author, first English writer on mineralogy.

*Torbern Olaf Bergman (Sweden), 1735–1784, chemist, founder of analytical chemistry, drew distinction and explained differences between pig iron, wrought iron, and steel.

*Henry Cort (England), 1740–1800, engineer, introduced puddling and the use of grooved rolls.

*Karl Wilhelm Scheele (Sweden), 1742–1786, chemist, anticipated Priestley's discovery of oxygen, discovered manganese (1774), chlorine, barium, and molybdenum.

*Martin Heinrich Klaproth (Germany), 1743–1817, mineralogist, discovered uranium (1789) and titanium (1794).

*Antoine Laurent Lavoisier (France), 1743–1794, chemist, creator of modern chemistry.

Johann Gottleib Gahn (Sweden), 1745–1818, chemist, isolated phosphoric acid.

*Claud Louis de Berthollet (France), 1748–1822, chemist, discovered composition of ammonia.

Fausto de Elhuyar (Spain), 1755–1832, chemist, first prepared metallic tungsten (1792).

William Reynolds (England), 1758–1803, patented (1799) the use of manganese oxide for steel manufacture.

John Dalton (England), 1766–1844, chemist, published table of atomic weights.

Jeremias Benjamin Richter (Germany), 1762–1807, chemist, invented alcoholometer.

*Louis Nicolas Vauquelin (France), 1763–1829, chemist, discovered chromium (1797).

David Mushet (England), 1772–1847, metallurgist, author, discovered black-band ore.

Sir Humphry Davy (England), 1778–1829, chemist, first isolated potassium and sodium.

*Jöns Jakob Berzelius (Sweden), 1779–1848, prepared pure iron, discovered selenium, thorium, and cerium, isolated silicon, and introduced the theory of allotropy.

Pierre Berthier (France), 1782–1861, chemist, wrote on metallurgical analysis.

Robert Sterling (Scotland), 1790–1878, patented regenerative principle (1817).

*Michael Faraday (England), 1791–1867, chemist and physicist, investigated the properties of iron and steel alloys.

James Beaumont Neilson (Scotland), 1792–1865, invented hot-blast (1828).

*Friedrich Wöhler (Germany), 1800–1882, chemist, discovered aluminium (1827).

Conservation.

I may add, although it may seem a truism, that the investigation of alloys of iron is exceedingly important and of great practical benefit and utility, not only from the point of view of obtaining the required combination for a given purpose, but also from that of obtaining for a given quantity of metal the maximum degree of utilization. As above alluded to, the world's resources in the matter of iron ores are not inexhaustible, and it may be incumbent upon us before long to more carefully husband them. The United States is now annually producing no less than thirty-three million tons of pig iron, Germany some twenty million tons, Great Britain, France, and Belgium nearly as much more, all involving enormous consumption of iron ore.* Quite apart from these two points of supreme economic interest the study of alloys, as I have already stated, is a most fascinating study and indeed a very wide one.

The rapid introduction of alloys of iron with other elements shows that they have met the necessity of the times. An alloy steel, although it is more expensive, is really an attempt at conservation ; it is possible to make a pound of alloy steel go as far as many pounds of ordinary steel.

As some amongst us have said that because other nations have now passed

* Diagram No. 1 shows the actual output of pig iron for 1912 as compared with the writer's forecast in 1905.

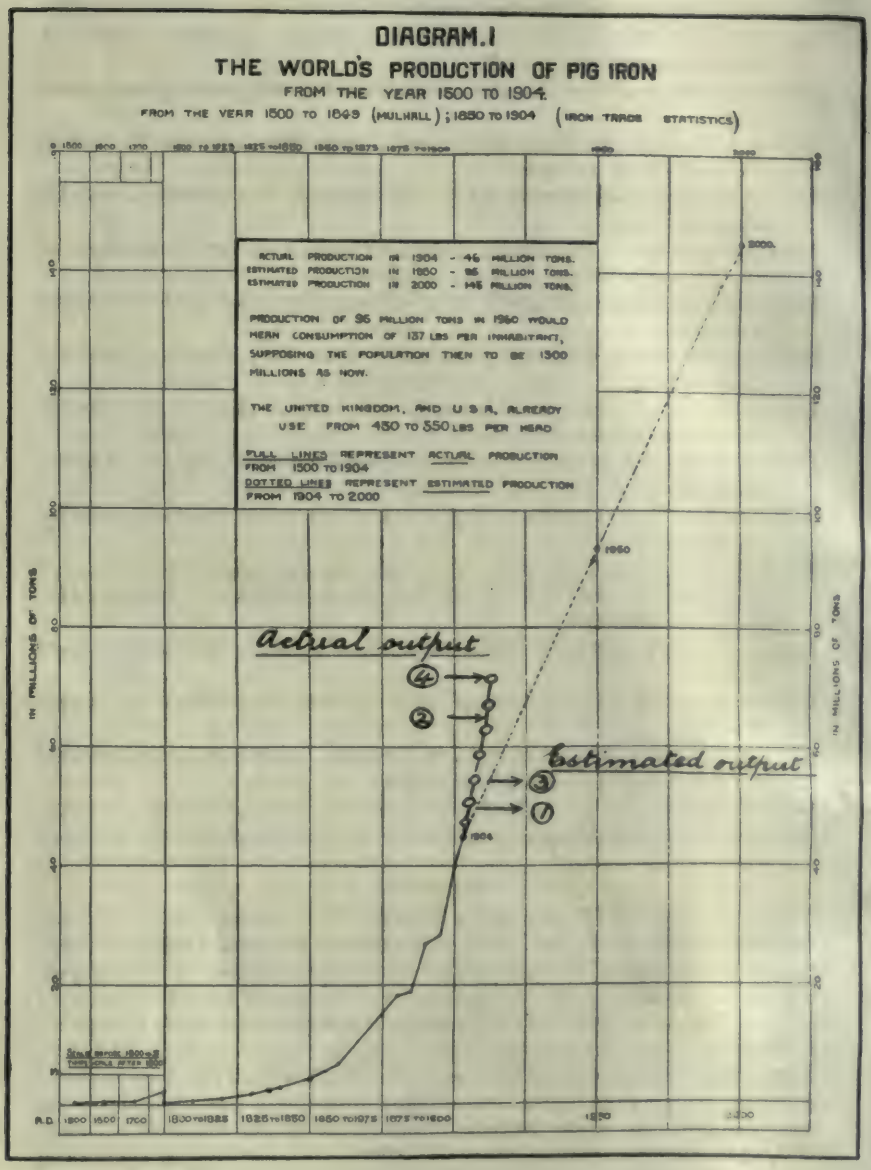


DIAGRAM. I
THE WORLD'S PRODUCTION OF PIG IRON
FROM THE YEAR 1500 TO 1904.
FROM THE YEAR 1500 TO 1849 (MULHALL); 1850 TO 1904 (IRON TRADE STATISTICS)
ACTUAL PRODUCTION IN 1904 - 46 MILLION TONS.
ESTIMATED PRODUCTION IN 1960 - 96 MILLION TONS.
ESTIMATED PRODUCTION IN 2000 - 146 MILLION TONS.
PRODUCTION OF 96 MILLION TONS IN 1960 WOULD MEAN CONSUMPTION OF 137 LBS PER INHABITANT, SUPPOSING THE POPULATION THEN TO BE 1300 MILLIONS AS NOW.
THE UNITED KINGDOM, AND U.S.A. ALREADY USE FROM 430 TO 550 LBS PER HEAD
FULL LINES REPRESENT ACTUAL PRODUCTION FROM 1500 TO 1904
DOTTED LINES REPRESENT ESTIMATED PRODUCTION FROM 1904 TO 2000
IN MILLIONS OF TONS
A.D.
1500
1600
1700
1800 to 1825
1825 to 1850
1850 to 1875
1875 to 1900
1900
1950
2000
1904
actual output
estimated output
4
2
3
1

Five Years' Comparison (1905–1910 *inclusive*)—

(1) In 1905, Hadfield estimated probable output for 1910 of ... 40 million tons.
(2) The actual output for 1910 was ... ... 65 million tons.

Seven Years' Comparison (1905–1912 *inclusive*)—

(3) In 1905, Hadfield estimated probable output for 1912 of ... 55 million tons.
(4) The actual output for 1912 was ... ... 72 million tons.

us in our output of iron we must be decadent, it is hardly necessary to point out that, notwithstanding our having gone to the third place from the production point of view in pig iron, we were never so prosperous as to-day. Therefore the mere tonnage production is not entirely an index, so long as we have cheap sources of supply where the ore or the pig or bar iron can be obtained.

It must be remembered, too, that as in the past the production of iron by different countries must vary from time to time. The country leading at one period may not necessarily do so for all time. The great and leading point is to provide for a source of supply of the ore.

The well known French writer Henri Gaston, in his interesting brochure, "Où va l'Allemagne," points out that Germany will in the near future exhaust her own supply of iron ore, then what is she going to do? She controls no outside sources of any great value. Without introducing politics, perhaps there was more than met the eye in Germany's interest in Morocco, with its great stores of iron ore. Gaston claims that France has a much greater and more certain metallurgical future. He goes so far as to say, "Nous sommes destinés, si rien ne vient contre carrer nos desseins, à devenir la nation métallurgique la plus puissante du monde." I have written these few remarks to show that any temporary heading of the list of nations producing pig iron cannot by itself alone be considered. There are many other factors.

French Metallurgy in the Eighteenth and Nineteenth Centuries.

Two remarkable books were published in 1846, one "L'Art de Tremper les Fers et les Aciers," by M. Camus, and the other "Mémoire sur la Fabrication et le Commerce des Fers à Acier dans le Nord de l'Europe," by M. F. le Play, Ingénieur en chef des Mines, Professeur de Métallurgie à l'Ecole Royale des Mines. That by M. Camus, who is described as "Ingénieur-Manufacturier, membre de la Société d'Encouragement pour l'Industrie nationale, ex-Ouvrier Contre-Maitre et Directeur-Fondateur de plusieurs Usines et Manufactures métallurgiques en France," deals in a most practical way with the methods required to obtain the best qualities from steel which has to be hardened and tempered. Much of the information he gives is quite as applicable to-day as when it was first written. He furnishes particulars of various temperatures as they were then estimated by the Wedgwood pyrometer, heat colours, and other information. I reproduce one of his tables in full (Table I), as it shows the care and attention then bestowed by this French expert. This list was published in 1846, showing that excellent work had even then been done with reference to the determination of high temperatures.

Turning to the work by Professor le Play, this writer shows how for a hundred years or more French metallurgy, as regards the production of high-class steel, had been entirely misdirected by the idea to which the French metallurgists obstinately clung for so long, that it was possible to produce in France bar iron for making steel of the same quality as produced by Sweden, this too in face of the wonderful progress then made by the English steel-makers, who had wisely adhered to the importation of high-class Swedish irons.

This book has for the first time made me aware that Réaumur * (by his elaborated researches published from 1720 to 1722), although a great scientist in many ways, made a terrible mistake, which hampered French industry for a long period, when he proved to his own satisfaction as he

* One of Réaumur's well-known books was "L'Art de convertir le Fer forgé en Acier" (Paris, 1722).

TABLE I.

Centifeux.	Détail, Couleur des Chaudes.	Millifeux.	Correspondance Thermomètre centigrade. Fraction négligée.	Pyromètre de Wedgwood.
1	2	3	4 *	5
Degré.		Degrés.	Degrés.	Degrés.
0	EAU bouillante, ZINC, état de ductilité pour son laminage	0	100	—
„	REDRESSAGE à la presse des objets trempés Maximum de chaleur	3	153	—
„	ETAIN, son premier point d'entrée en fusion	6	206	—
„	Jaune-PAILLE, première recuite de trempe (sèche)	7	224	—
„	Id. d' OR, deuxième id. (moins)... ...	8	242	—
„	GORGE-DE-PIGEON, troisième id. (moins) Entrée en fusion du Bismuth ...	9	260	—
1	VIOLET, quatrième id. (moins)	10	278	—
„	Bleu-FONCÉ, cinquième id. la plus douce à donner...	11	295	—
„	PLOMB, il entre en fusion à forcée ...	13	330	—
„	MERCURE, id., à forcée	15	366	—
„	ZINC, id., à forcée...	16	384	—
„	Expiration forcée de la trempe, à cette chaleur il y a recuit	17	402	—
„	ANTIMOINE, il entre en fusion à forcée à	19	437	—
„	Rouge-BRUN, rien pour la trempe, recuit de petits objets à la forge	27	579	O_{580}
„	ARGENT, il entre en fusion à	108	2,018	20
11	LAITON, id., à	112	2,089	21
14	CUIVRE, id., à	137	2,533	27
16	OR, id., à	157	2,888	32
18	Rouge-CERISE, à	185	3,196	39
22	Rouge-VIF, à	226	4,114	49
26	Rouge-CLAIR, à	262	4,753	58
30	Rouge-ROSE, à	299	5,410	67
33	Rouge-BLANC. Au feu de forge de faibles étincelles partent des angles du fer, à	335	6,049	76
35	BLANC PUR, maximum d'éprouvette, fin de cémentation (fabrication d'acier) à	351	6,334	80
40	Premier BLANC-SUANT, soudure du fer tendre, carburé, à	400	7,204	92
41	Deuxième BLANC-SUANT, à goutelettes métalliques, soudure du bon fer ordinaire, à	412	7,417	95
43	Troisième BLANC-SUANT, id., soudure du fer très-pur, à	430	7,736	99
51	FONTE GRISE, au creuset, première fusion agglutination (réunion) à ...	513	9,211	120
55	ACIER de cémentation au creuset ; il entre en fusion à	554	9,939	130
57	FONTE GRISE, id., en état de bain, à ...	570	10,222	134
58	FER, il entre en fusion pleureuse, à ...	574	10,294	135
59	ACIER de cémentation, maximum du bain, à	586	10,507	138
60	MINERAI, état de bain (Haut-Fourneau), à	595	10,667	140
63	FER, il y a agglutination (réunion), à ...	635	11,378	150
65	Id. état de bain, à	655	11,733	155
67	Id. No. 1, maximum du bain, à ...	676	12,106	160
70	Id. très-pur, id., à	700	12,532	166

* As some of the figures in column 4 are so high, probably M. Camus had the Fahrenheit scale in mind. Even then the figures are of course entirely incorrect in the light of our present knowledge.

thought that it would be possible to treat irons made in France so that their quality would be equal to the pure products of Sweden. Owing to his misapprehension of the true conditions attaching to the production of high-class steels very large sums of money were lost in France both under the Monarchy and the Republic. This shows how exceedingly careful a scientific man should be in advancing theories not fully tested and confirmed in practice.

The position which had already then been reached by Sweden is but another proof of the debt of gratitude the metallurgical world owes to that country. As Professor le Play said in 1846 (p. 91):

"For two centuries the Swedish metallurgists have exploited with great cleverness the steel-making quality of their minerals. This branch of the metallurgy of iron is due to their efforts.

"Understanding that the success of cementation steelworks rests essentially on the confidence which the manufacturer may feel in the raw material, they have made every individual and collective sacrifice which the scrupulous maintenance of the qualities represented by the trade marks necessitated. Hence, for example, the establishment of these 'Jern-Vågen,' model institutions for all commercial people, which, by a rigorous control over the quality of the products, guarantees the entire industry of the country against the divergences which might be prompted by private interests. It is, therefore, to the intelligence and the commercial integrity of the Swedish ironmasters, no less than to the genius of Yorkshire manufacturers, that is due the expansion of this new art, which, placing henceforth the steel industry within the means of every nationality, has come to subserve one of the most pronounced tendencies of modern society, and which, by a large output of steels of greater perfection and above all harder than the natural steels, has endowed our civilization with means of action proportionate to the magnitude of the control which it exercises over matter and to the greatness of the results it seeks to attain. The facts revealed in this paragraph prove that Swedish metallurgists have been able to place themselves, so far as they are concerned, at the head of this noble mission, while everything appears to indicate that they will know how to maintain that position."

Professor le Play points out (p. 99) how it was that Réaumur, clever as he was, had gone wrong:

"The disastrous results from which the French steel industry suffered, by following the advice of Reaumur, did not change the opinion of the practicability of the process, although based merely on laboratory experiments. The most distinguished scientific men and the most eloquent writers persisted in maintaining that French iron was very suitable for steel making, and the Government, much influenced by their arguments, continued to insist on the use of this iron as a condition in making any grant to assist any infant industry."

Works after works in France came to grief owing to the obstinacy with which the French clung to their methods of trying to utilize their own empire's products at the expense of quality. Even when works were started, as for example those of Aciéries de Nerouville in 1770, where Swedish iron was exclusively used, special pressure was brought to bear to compel them to discontinue using the imported product, researches being renewed in order to try and utilize French iron, again only with the same disastrous consequences.

Professor le Play further points out (p. 132):

"As I have already said, if Réaumur, in 1722, had not misled those engaged in the industry, it would have developed, as in England, by using Swedish iron. It would have done it with probable success, since, during the whole eighteenth century, England believed it should lay taxes on the right of importation of foreign iron."

I have given the foregoing at some length because it is interesting to see that our British common sense and our practical way of regarding matters of this kind kept us on the right road. It was good judgment of no little value, for it resulted in Sheffield becoming the centre of the special steel trade of the world, a position which it still holds. The French idea was that the quality of the material then known as "body" was to be obtained by purifying the products of their more imperfect ores. But as we all know, this was not practicable, and Sweden still holds its position in the world for the production of the purest quality of raw material. There is more Swedish pig and bar iron now being used than at any previous time.*

Le Play also mentions, and I think this is specially interesting in view of Faraday and Stodart's experiments in 1820, that these commenced owing to Faraday's having analysed certain specimens of material from India known as Wootz steel. A similar series of experiments were then undertaken in France. Assistance was given to the project by the well-known Société d'Encouragement pour l'Industrie Nationale, a Society still existing and doing most excellent work. This Society found the necessary funds for carrying out some three hundred experiments upon alloys of iron with different metals. A report on this subject was presented to the Society in 1821. The experiments were continued to the year 1824, but did not appear to result in any manufacturing benefit. The Société d'Encouragement pour l'Industrie Nationale then granted gold medals to several investigators in the art of steel-making.

Value of Research.

Let us remember that it is to the valuable properties of the many alloys of iron now made, from carbon steel to the complex one known as high-speed tool steel, which contains no less than five different elements apart from the iron itself, is due the remarkable progress we have made, whether in the arts of peace or war. I will give one simple concrete instance—the modern motor vehicle, whether for private or trade use, with which such an enormous traffic is now carried on with so great convenience and comfort to the public of all lands. Take away the alloy steel used in its construction, and it could no longer be produced. The combination of lightness and strength necessary in such modern products is only possible by the use of special alloy steels.

To study the qualities of alloys of iron with other elements involves much research work, which is a noble occupation for mankind. Whilst this work may not appear so attractive as the discovery, for example, of a new element, it is not less important. The value of research work was early recognized in this country, for in the very interesting *History of the Royal Society of London for the Improving of Natural Knowledge*, published in 1702 and written by "Tho. Sprat, D.D., Lord Bishop of Rochester," it is said in the Preface or Dedication portion to the King, Charles II.:

"Of all the Kings of *Europe*, Your Majesty was the first, who confirm'd this Noble Design of *Experiments*, by Your own Example, and by a Public Establishment of the Royal Society. An *Enterprise* equal to the most renoun'd Actions of the best *Princes*. For, to increase the Powers of all Mankind, and to free them from the bondage of Errors, is greater Glory than to enlarge *Empire*, or to put Chains on the necks of Conquer'd *Nations*. A higher degree of Reputation is due to *Discoverers*, than to the *Teachers* of *Speculative Doctrines*, nay even to *Conquerors* themselves. Nor has the *True God* himself omitted to show his value of *Vulgar Arts*.

* Plate IV. is a photograph from an engraving of Sheffield in the year 1745 when its population was about 42,000, now increased to about 460,000. Plate V. is a photograph from an engraving of Sheffield in the year 1819.

PLATE II.—PORTRAIT OF BENJAMIN HUNTSMAN'S SON.

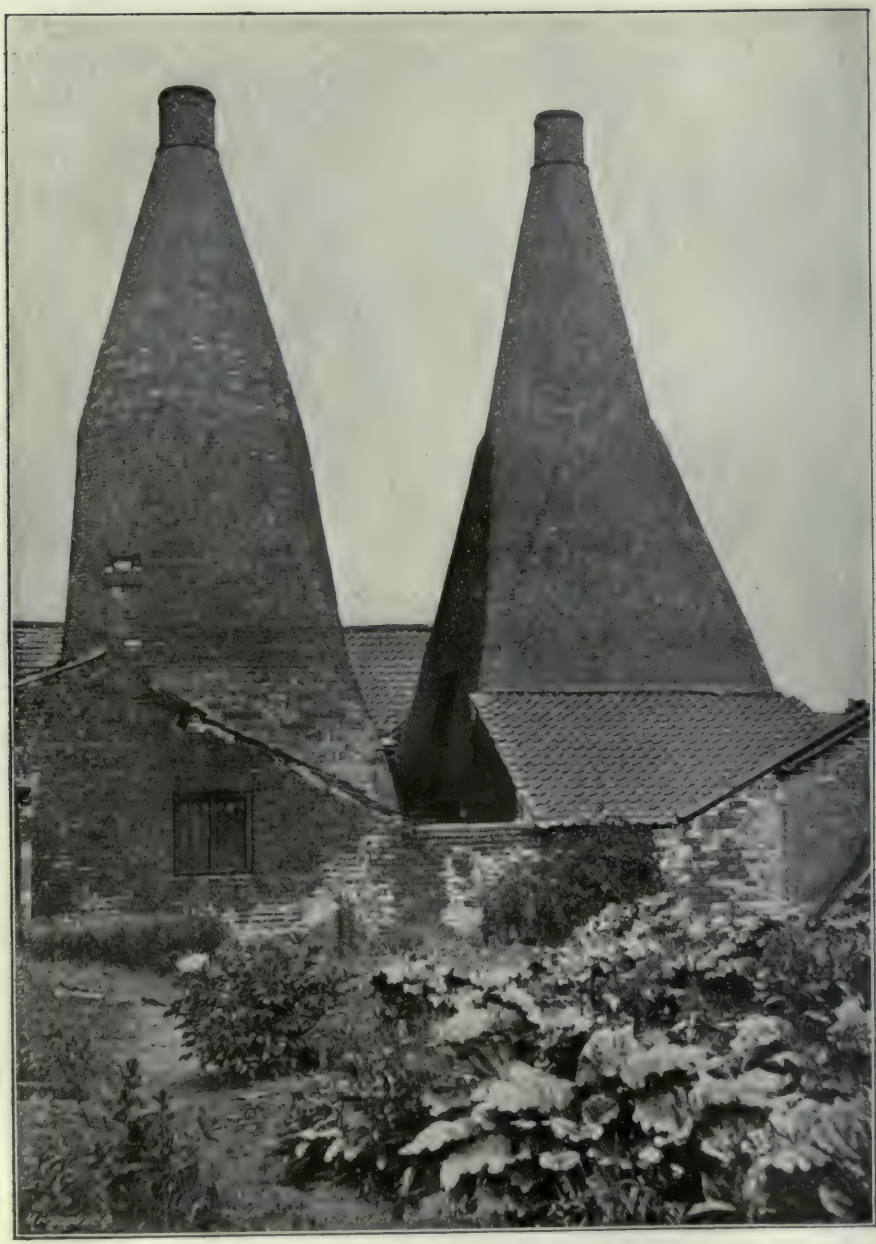


PLATE III.—CEMENTATION FURNACES BUILT BY BENJAMIN HUNTSMAN ABOUT 1750.

Plate IV.—The East Prospect of Sheffield, in the County of York (A.D. 1745).

Sheffield or Sheafield stands in the Southern part of the West Riding of Yorkshire where the two Rivers Dun and Sheaf meet, to which last it owes its Name. This Town was anciently famous for making the Iron heads of Arrows, and is celebrated by Chaucer 300 years ago for the Blades of Knives worked there; by degrees it hath much Improved in all manner of Cutlers ware. Its Situation is delightful and somewhat uncommon, it being seated on a Round Hill in the Midst of a Valley, which is surrounded by many higher Hills. This supplies it with many valuable Falls of Water necessary for carrying on the Manufacture of the Place. This Advantage of Streams to turn their Mills, together with great plenty of Coal in its neighbourhood render it perhaps the fittest place in the Kingdom for the Business which is here carried on. It had a very strong Old Castle which belong'd to the Lovetofts, the Lords Furnival; and the Talbots, Earls of Shrewsbury. In which Mary Queen of Scots remain'd a Prisoner for 16 or 17 years under the Custody of George Earl of Shrewsbury. This Castle was built in the Reign of King Henry III and after the death of King Charles I was demolish'd. Here is a market every Tuesday and Thursday. Fairs, one on Tuesday after Trinity Sunday, and another on the 17th November. The Mannor of Sheffield which extends in length 18 miles and in breadth upwards of 8 miles, did formerly belong to the Earls of Shrewsbury; but now to his Grace the Duke of Norfolk.

1. Broomhall.
2. St. Paul's Chappel.
3. Road to Manchester.
4. The Town Hall.
5. Trinity Church
6. London Road.
7. Hospital founded by Gilbert Earl of Shrewsbury.
8. Castle Hill bowling-Green.
9. Lady's Bridge.
10. River Dun.
11. Bridge Houses.
12. The Duke of Norfolk's Nursery Garden.
13. Park Hill where this Drawing was taken.

PLATE V.—ENGRAVING OF SHEFFIELD IN THE YEAR 1819.

In the whole *History* of the first *Monarchs* of the World, from *Adam* to *Noah*, there is no mention of their *Wars*, or their *Victories*: All that is Recorded is this, They liv'd so many years, and taught their *Posterity* to keep *Sheep*, to till the *Ground*, to plant *Vineyards*, to dwell in *Tents*, to build *Cities*, to play on the *Harp* and *Organs*, and to WORK IN BRASS AND IRON. And if they deserv'd a *Sacred Remembrance*, for one *Natural* or *Mechanical Invention*, Your *Majesty* will certainly obtain *Immortal Fame*, for having establish'd a perpetual Succession of *Inventors*."

Quaint as may seem these words to us of to-day, there is indeed still now as great truth in them as when they were uttered. The marvellous recent progress of the world has been largely due to the scientist, to the inventor, and not least in these branches of human thought are those who work in "natural or mechanical invention," or, to use again the Bishop's words, "in brass and iron," though nowadays the latter metal plays the more prominent part.

Since the date when these wise words were uttered the Royal Society has seen one long-continued career of success, and owing to the devotion of its Fellows to the cause of science and scientific progress, mostly without reward of any kind, there is no country where science and scientific work is more highly esteemed than in Great Britain. I know it is often customary to say that we lack appreciation of scientific merit, but I do not believe it. The fight for the cause of advance may be severe here, but in the end we English recognize to the full true merit. We need not be ashamed when from this little island have come—not to mention those still with us—such men in the Anglo-Saxon race as Bacon, Newton, Priestley, Dalton, Boyle, Cavendish, Faraday, Davy, Huxley, Tyndall, Spencer, Darwin, Kelvin, Percy, Roberts-Austen, and many others. On the more technical side, Dudley, Sturtevant, Pettus, Huntsman,* Darby, Kirwin, Cort, Heath, Heaton, Mushet, Bessemer, Siemens, Bell, Whitwell, also many others in the Old World. In the New World, such men, as regards both classes of research, as Benjamin Franklin, Fulton, Agassiz, Willard Gibbs, Rowland, Barus, Edison, Bell, Steinmetz, Sterry Hunt, Howe, Holley, Fritz, and others who are referred to in the earlier part of this address.

The foregoing list is necessarily a very incomplete one and refers only to the workers in the Anglo-Saxon race. It, however, represents at any rate some of those who have done the greatest work in the domains of the sciences of chemistry, physics, electricity, engineering and metallurgy.

Our Society in execution of its own smaller, but, I think, laudable programme has always endeavoured to contribute to the increase in the general stock of human knowledge, and our very title is an earnest that we, like Faraday, are searching for information regarding unknown phenomena with a view to a general increase in the comfort and progress of mankind.

The Author's Research Work.

At the time I first started my own research work, in 1882, little was known on the subject of alloys of iron. In fact, in the light of our present knowledge, one might safely say that the subject was practically an unknown one.

Mars, the eminent German writer, in his recent book *Die Spezialstahle*, has been good enough to say: "The most extensive experimental researches, which may be said to have laid the foundation for entire knowledge of steel alloys, were carried out by Hadfield in the eighties of the last century. . . . His two works on manganese steels and silicon steels have become of decisive importance as regards the development of the technics of steel alloys. They

* Whilst no portrait is extant of Benjamin Huntsman, Plate II. is that of his son Plate III. shows the cementation furnaces built by Benjamin Huntsman about 1750

not only supplied a wealth of important facts from the purely scientific point of view, but they subsequently led up to the evolution of many new qualities of steel. . . . The first thorough researches concerning silicon and iron alloys which could claim to have investigated the properties of silicon steels from the standpoint of the steel manufacturer, with a view to the uses of the alloys examined, were published by Hadfield. This work was the second of the series of publications forming the foundation of the entire modern knowledge of alloys of iron."

Pourcel, the distinguished French metallurgist, said that he "considered the production of manganese steel the most important event in practical metallurgy during the last ten years, and which might take its place beside the result of the labours of Gilchrist, Bessemer, Siemens, Martin, and Mushet." *

Dumas, in his *Recherches sur les Aciers au Nickel à Hautes Teneurs*, said that my alloy studies were "the first publications which had been made upon alloys containing high percentages of elements other than iron."

Bradley Stoughton, in his excellent work *The Metallurgy of Iron and Steel*, was good enough to make similar comments.

Finally, Osmond, the great French scientific metallurgist, said that my discovery of manganese steel was of the same order and equalled in importance the discovery in past centuries of the effect of quenching upon carbon steel.

I have referred to these quotations in order to show the truth of my earlier remarks, that when first starting my labours in the eighties of the last century the general knowledge available on this subject was very small indeed.

In this connection I should like to add that the conception which formerly ruled in regard to the term "alloy" prevails to this day in the mind of the general public. An alloy to many implies nothing more than the addition of a baser metal to a finer one, the object of the mixing of the two together being to obtain a cheaper commercial article and one that will wear better. This, we all know, is not at all the case in regard to special steels and special steel alloys or combinations of the present day. The definition of the word "alloy" might better be made to read "the combining by fusion of two or more metals together, or of a metal with one or more metalloids, for various specific purposes."

Metallurgy in the Middle of Last Century.

A most valuable work was issued in 1867, Kohn's *Iron and Steel Manufacture*, the best of its kind for almost a generation, and for the origin of which we have largely to thank those who have given us the modern and most valuable technical journal known as *Engineering*. This served as a text-book for over twenty years, and now remains of much historical interest. This book gave amongst its 270 pages not more than about half a dozen references to metallurgical papers. How little this seems when compared with the special literature now available! Take, for example, the well-filled *Journals* of the Iron and Steel Institute, containing as they do annually about one thousand pages of original matter, being the reproduction of about thirty papers with the discussions thereon, and about five hundred pages more of notes showing the progress made in the home and foreign iron and steel industries; they

* Plate VI. is an extract from the Author's experimental book, dated 7th September, 1882, showing the entry relating to his first researches which resulted in the discovery of Manganese steel.

7/9/82 T.1 6 " 23/9/82

Was bd to make the fo
to making a n. hard steel
& some very curious re
momentous results that ma
metallurgical opinions as

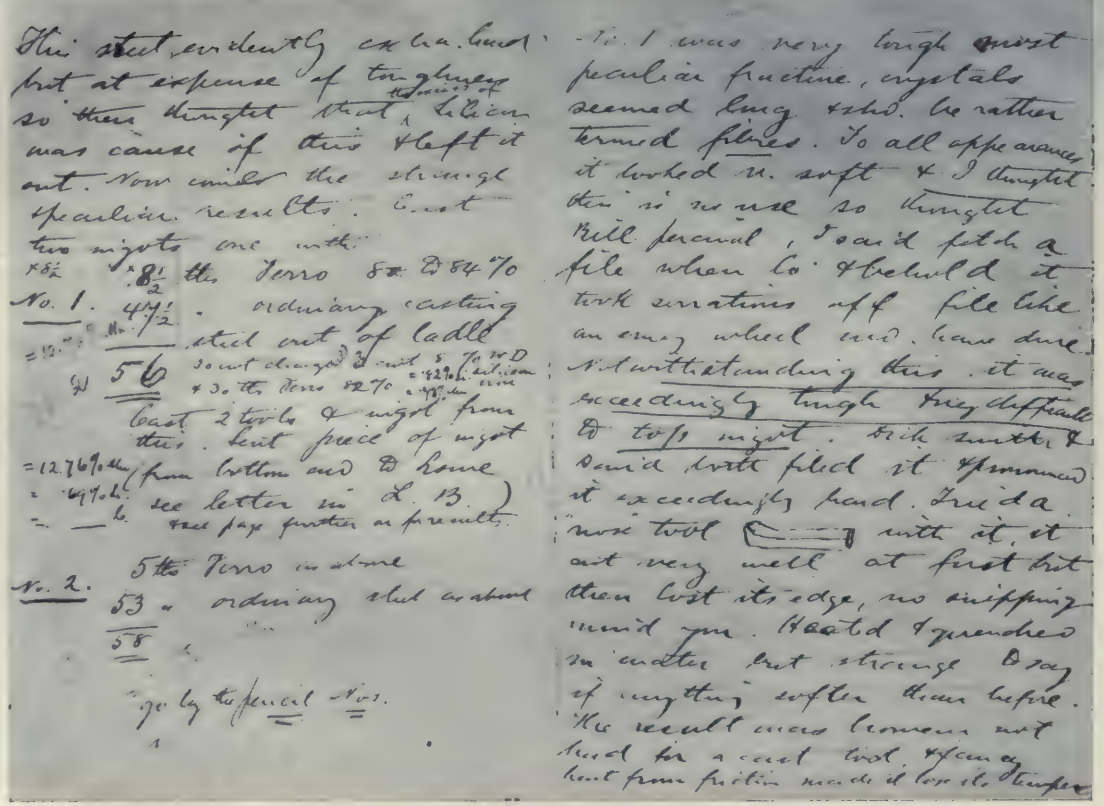
On 7/9/82 cast an ingot
also cast an ingot shell
die, two tools, & 2 nail
cutters (see further on).

cast a 7¼" & 4½" nail-c
grinding off fashes) sent
testing. The large cutter weigh
ordinary cast steel stuff, melted in pot
but with hammer. Beautiful cla
it and not grind. V. smooth
plent of flux, to hard that
it spoilt half a doz
with a file instead o
than drilled metal, made tw
melted in pots. It cut a remar
hole when trying in mort cast

louring or pots. with a recess
for rounds, the bars bd
etc perhaps must
& some extent quite alter
& alloys of iron & steel.

with 4 lbs of 8% 0 84% Iron
49 " W. D. 8% Silica
41 " Clown iron
99 - 7.45 % Mn.
- 3.96 % Si

seemed n. hard when
them & Eliza Tinsley for
2 oz. less than a cutter of
much sharper note when
note. Tried once when hot
casting 2" 1 — 12 — 7 14 solidified well
when dipping off runner
chisels & cutg. Dared tried it
found it was nice boarder
tools from a piece of scrap
off 6" d.a., edge perfect, but
bd. mil hammers, crumbled it



This steel evidently exhausted but at expense of toughness so that tungsten steel, Silicon was cause if this & left it out. Now under the strange & peculiar results. Cast two ingots one with

× 8½ × 8½ lbs Ferro 8% D 84%
No. 1. 47½ ordinary casting
= 12.76% 47½ steel out of ladle
(2) 56 so not charged 3 cut 5.76% W D
+ 3 lbs Ferro 8.2% = 2.28% silicon
cast 2 ingots & right from this last piece of right
= 12.76% (from bottom and D home
= 47% see letter in L. B.)
= — lb. two pages further on for results.

5 lbs Ferro in alone
No. 2. 53 " ordinary steel as above
58

go by the pencil Nos.

-ti. I was very tough & most peculiar fracture, crystals seemed long & rhd. be rather termed fibres. To all appearances it looked v. soft & I thought this is no use so thought will forward, I said fetch a file when Co. & they did it took ever times off file like an emery wheel and leave dust. Notwithstanding this it was exceedingly tough very difficult to top right. Dick smith & David both filed it & pronounced it exceedingly hard. Tried a [illegible] tool with it, it cut very well at first but then lost its edge, no chipping round you. Heated & quenched in water but strange D say if anything softer than before. The result was lemons not fit for a cast tool & came out from [illegible] made it lose its temper

PLATE VI.

afford an illustration of the huge step forward which has been made in this direction since the sixties. The *Journals* of this Institute, devoted as they are to ferrous metallurgy, have now entered upon their eighty-eighth volume, besides which there have been issued from time to time a number of extra volumes devoted entirely to the reproduction of the Carnegie Scholarship memoirs. The Iron and Steel Institute, like our Society, had small beginnings; it has developed into a most powerful body, and one whose influence is felt the world over. To its able Secretaries, Mr. J. Stephen Jeans in the past, now gone from us, and to-day Mr. G. C. Lloyd, the metallurgical world is greatly indebted.

With reference to the work of the Institute I would remind members of our Society that a number of Carnegie Scholarships are yearly granted by the Council of the Iron and Steel Institute. The applications for these scholarships are very numerous from the Continent and America, and none too numerous from those in this country. I wish our younger members would come forward and show that they either are making research or wish to do so, so that the Council of the Iron and Steel Institute may be able to give a still larger share of these valuable scholarships to those in this country.

There is ample room for our Society to develop its own special work by the side of other Institutes. The *Transactions* we also have issued since 1903, the date of our foundation, form a not unimportantcontribution to the world's literature on the special scientific subjects, chiefly relating to electrometallurgy, with which we deal. It would seem that there is ample room for our Society to develop its work quite apart from that done by the Iron and Steel Institute, as we do not touch or interfere with the scope of their work.

Steel Alloys Research.

As regards steel alloy research apart from carbon steel—though even the latter might also be included, as so comparatively little was known concerning it but fifty years ago—after carefully looking through the pages of Kohn's book above referred to very little evidence can be traced of work having been done in this direction. I have specially selected this book, as a starting-point as it were, because it represented at the time and for many years after its publication, in 1867, a very complete illustration of the practical side of thought which then prevailed. At that period no one appeared to have given very much thought to the effect which numerous elements can have upon iron and to the possibilities in store for various alloys obtained by combining them with iron. In its 270 pages, forming a very complete treatise on siderurgy and mechanics, I cannot find a glimmering of that enormously important development which was to be due to alloy steels.

I use these last words advisedly to depict the situation then existing compared with what obtains at the present day, and, as already pointed out as further illustrating the point, taking one branch of progress alone, the manufacture of a motor-car, if you take away special alloy steels that manufacture becomes an impossibility. Further, without special steels our battleships would still be provided with a protective covering of a quality only equal in resistance to that of the first armour-plated ship, *La Gloire*, and would be, comparatively also, quite as ineffective as the latter as far as offensive power is concerned, but even this great advance of iron plates only occurred about fifty years ago.

Kohn, in his excellent article devoted to the subject of ferro-manganese, a product of such great importance to the world's steel-makers, does say that "steel-makers are now entirely dependent upon spiegeleisen, which gives

good results, but they recognize the want of a richer manganese alloy, and this will probably make itself felt all the more when the attention of Bessemer steel makers is more largely turned to the manufacture of armour-plates." But in thus speaking of a "richer manganese alloy" Kohn had evidently in mind the action of manganese in the carrying out of the Bessemer process. He was thinking of the solubility of ferrous oxide in the bath and its attendant disadvantage, namely, that of yielding a metal saturated with the oxide, a disadvantage which is done away with by using manganeseous iron, the manganese reducing the oxide when it remains unreduced by the silicon, the carbon, or the phosphorus, and protecting the metal against a saturation of ferrous oxide. Kohn's remark on this point was written in 1867. That is hardly fifty years ago, and it was not until some twenty years later, by the combination of scientific research with every-day work practice, that the "richer manganese alloy" he referred to was developed in the shape of ferro-manganese. I well remember that in the year 1886 down in Sheffield we paid as much as £120 per ton for ferro-manganese of quite indifferent quality, judged on the standard of to-day, containing about 60 per cent. of manganese, and were glad to get even that.*

Science and Practice working together.

To-day ferro-manganese of very high quality, containing from 80 to 84 per cent. of manganese, can be obtained at under £10 per ton. This speaks volumes in favour of what science and the mutual working together of science and practice can achieve. In this connection I cannot help referring again to the admirable way in which the leading metallurgical Society, the Iron and Steel Institute, has fostered this combination of the two, not in this country alone, but universally. As was pointed out at the Spring Meeting in 1912 by Mr. A. Greiner, the now able President of that Institute, "twenty-four nationalities were represented within it, from which he thought it would be agreed that science recognized no boundaries of nationality or of race. They worked together not only for the good of the particular country to which they belonged, but for the advancement of scientific knowledge in the world at large." I trust that this Society can lay claim to be trying to do its quota of research work. We may count less in numbers than our larger Societies; our formation has, however, only been of comparatively recent date.

Incidentally, as showing the wonderful advances which the studies of the metallurgical engineer have made possible, the following interesting fact may be referred to. Although an astonishing statement, it can be accepted as correct, as the figures were given to me by an expert: namely, that assuming the cost of pig iron in America is about $14 per ton at the furnace, and excluding certain charges of comparatively small nature, then on this figure

* The following represents the analyses of two lots of ferro-manganese with which some of my early experiments were carried out in the year 1883:

Made by	C.	Si.	S.	P.	Mn.
Terre Noir Company (France)	6·0	0·65	—	0·123	81·60
Pyle & Blaina Co. (South Wales)	5·8	0·67	0·02	0·23	81·50

Since the above date the quality of ferro-manganese has been much improved, and the modern product would contain less phosphorus and less silicon.

of $14 per ton the cost of labour is only about 36 c. This result is obtained largely by the ingenuity and skill of the metallurgical engineer.

To put it another way, the approximate cost per ton of pig iron has been estimated as follows:

Coke	$2.00
Ore	5.00
Limestone	1.00
Assembling coke, ore, limestone	5.00
Supplies	0.60
	$13.60

This leaves only 36 c. to 40 c. per ton to pay the bill for the human labour employed in the production of one of the first necessities of life, "pig iron," including in this term the product of the blast furnace.

Development of Research during the last Fifty Years.

In regard to the alloys of iron with other elements than carbon, this field of research, the development of which I claim without fear of contradiction to be one of the most marvellous of the many extraordinary developments of the last fifty years, was indeed a narrow one even so near our time as the sixties and seventies of the last century. As showing how scanty was the metallurgical literature of those days, even as late as 1870 Sir William Crookes, F.R.S., who was joint author with Dr. Ernst Röhrig of an adaptation of Professor Kerl's *Practical Treatise on Metallurgy*, says (vol. 3, p. 9): "There are very few published works on the manufacture of steel: the following treatises are those most worthy of mention:

"Dammemme: practisches Handbuch der Stahlbereitung; deutsch von Hartmann, 1839.

Overmann: die Bereitung und Verarbeitung des Stahls, deutsch von Hartmann. 2 Auflage, 1856.

Gruner et Lan: état présent de la Métallurgie du fer en Angleterre. Paris, 1862.

Jullien: Handbuch der Eisenhüttenkunde, deutsch von Hartmann, 1861.

Tunner's Abhandlungen im Leoben. *Jahrbuch.*

Schafhautl's Artikel über Stahl, in Bd. XV von Prechtl's technologischer Encyklopädie.

Landrin: Traité de l'acier. Paris, 1859.

Dessoye: Etudes théoretiques, etc. Paris, 1859."

It is curious to note that there is no reference here to Dr. Percy's *Metallurgy*. On the other hand, the book may not then have been well known. Contrast this with the admirable and very full metallurgical literature available to-day!

An extract from the *Practical Treatise on Metallurgy* in question reads as follows. It deals, as will be seen, with iron and carbon alloys exclusively. The extract is from vol. iii. ("Steel, Fuel, Supplement"), pp. 21, 22:

"Ever since the Swedish chemist, Bergmann, in the second half of last century, called attention to the part which carbon plays at the formation of different kinds of iron, steel has been considered as a combination of iron with, in certain limits, a variable proportion of carbon, which proportion, and its more or less uniform distribution, influences the quality of the steel: this view is still very frequently entertained.

"Accepting this view, Gurlt (*B. u. h. Ztg.*, 1860, p. 502; *Berggeist*, 1860,

No. 19) considers steel as a combination of Fe8C + Fe ; Tunner (*Leob. Jahrb.*, 1861, x. 480) as a combination of Fe4C + Fe ; Lohage (*Zeitschrift des Vereins deutscher Ingenieure*, 1857, p. 268 ; *B. u. h. Ztg.*, p. 48 ; *Berggeist*, 1858, p. 14) as certain combinations of carbon (Fe12C, Fe20C, Fe28C) consisting of tetrahedral molecules which admit of hardening, in opposition to compounds forming octahedral molecules which cannot be hardened.

"Mayrhofer (*Leob. Jahrb.*, 1861, x. 437) has suggested the following chemical formulæ for different kinds of steel :

	Formula.	Fe.	C.	Fe.*	C.*
Hard natural and cast steel	Fe6C	98·16	1·84	96·55	3·45
Cast and shear steel, not fit for springs and wire owing to its brittleness	Fe7C	98·42	1·58	97·03	2·97
	Fe8C	98·61	1·39	97·39	2·61
	Fe9C	98·77	1·23	97·67	2·33
	Fe10C	98·89	1·11	97·90	2·10
Cast and shear steel elastic and fit for springs and wire	Fe11C	98·99	1·01	98·09	1·91
	Fe12C	99·06	0·94	98·25	1·75
	Fe13C	99·14	0·86	98·38	1·62
	Fe14C	99·20	0·80	98·49	1·51
	Fe15C	99·25	0·75	98·59	1·41
	Fe16C	99·30	0·70	98·68	1·32
	Fe17C	99·34	0·66	98·76	1·24
Soft puddled steel and fine-grained iron	Fe18C	99·38	0·62	98·82	1·18

"Compounds below Fe18C can no longer be hardened and pass into wrought iron. According to Mayrhofer, welded Brescia steel of the composition Fe10C is more elastic than English cast steel of the composition Fe12C ; some English steel for clock springs has the composition of Fe11C or Fe12C, and some of this steel that from Fe15C to Fe17C.

". . . Fuchs (*Dingl. Bd.*, 158, p. 209 ; 1860, pp. 43, 124) seemed to be of the same opinion, and he considered the different crystallization as the essential difference between steel, wrought iron, and cast iron. He considered wrought iron as an aggregation of cubic crystals, cast iron as an aggregation of rhombohedral crystals, and steel as standing between the two : on hardening the steel, the cubes were transformed into rhombohedrons and on slowly cooling the reverse took place."

I have quoted this somewhat fully because the opinions expressed are not a little remarkable. It will be seen that the chemist of that day had formulated theories which at any rate to some extent were running in the direction in which modern research seems to be tending with regard to combinations of iron and carbon. It seems to me, too, that we have not followed up this particular direction of research as much as might have been the case.

Prize for Research Work.

This is a rich and profitable field for the younger chemist if he will devote his attention to this particular branch of chemical research. In fact, to show the importance I attach to this subject, I have suggested to the two leading Institutes in England and America, namely, the Iron and Steel Institute and the American Institute of Mining Engineers, that I am willing to offer a prize

* The formulæ for the different percentages of iron and carbon as now worked out do not seem to agree with the figures given by Mayrhofer. The columns headed by an asterisk (*) show the relative percentages as we work them out to-day.

of £200 for the best paper or research on this subject*—in other words, to continue the investigations with regard to the combinations of iron and carbon, and thus follow up the great work originated by Abel, Müller, and Ledebur. This competition is not confined to any particular country, but is international and open to all.

The following suggestions are also added for the guidance of those who wish to take part in this competition. While it is not desired to define too closely the exact lines or scope of the research, as it is advisable to make these as broad as possible, the object in mind may be said to be generally as follows:

To elaborate and find out the best methods of determining the forms of carbon in steel or iron, including those in iron alloys. A portion of the work would probably be a continuation of the researches which have in the past been carried out by Jullien, Abel, Müller, Ledebur, T. Sterry Hunt, Akerman, Arnold, E. D. Campbell, Stead, Hogg, Parry, and others.

In a generic way, metallurgists now speak of carbides, sub-carbides, double carbides, special carbides, and other combinations. It is very desirable that those should be accurately defined and understood.

It is also desirable to know whether there are other or new forms; if so, can these be separated and their characteristics obtained?

It may be interesting to point out that the carbon compounds now definitely known are stated to number over 80,000. It is very probable, therefore, that there is room for much valuable and useful research to be carried out with the object of increasing our knowledge of the various combinations of carbon with iron, as probably some of these are still unknown.

In addition to research work upon particular forms of carbide which have not yet been determined, it is also desirable and necessary to determine the state in which the carbon exists. For example, there exists what is termed a "missing form" of carbon, about which little is known or understood. More light is required about this form, as for many years very little has been added to our knowledge on this subject. It would be desirable, for example, to know whether the carbon not accounted for as carbide is "missed" in consequence of its being in so fine a state of division, or whether it is present in some special form or condition.

It may be mentioned as a general statement that when steel is in the austentic condition it is softer than when transformed to the martensitic formation. In the former, the carbon is considered to be in complete solution; yet steel showing martensitic structure is said to contain its carbon in complete solution also. If it could be shown that the martensitic formation results from the commencement of the falling out of solution of the carbon, this would be of great assistance to all those who are desirous to have increased knowledge in this direction. It is therefore desirable to know exactly in what state the carbon exists in the austentic and martensitic formations.

It is also necessary, if possible, to ascertain the molecular constitution of the carbides. Such a point has been raised by the able American scientist Professor E. D. Campbell, and much important research work has been carried out by him with regard to certain particular combinations or forms of carbide. In other words, is the ordinary carbide Fe_3C, Fe_6C_2, or is it some other combination? If so, what is its nature and molecular constitution?

The above seems to be an outline of the general direction which should guide those considering and taking part in this research. It is hoped that the results obtained will throw much light on the cause of the hardness of steel, also the nature and form of carbon combinations with iron and its alloys.

* Since writing the foregoing, the offer has been accepted; full information can be obtained from the Secretaries of the two Institutes in question.

It may be mentioned that no special conditions are imposed as to the length of competing manuscripts (although diffuseness and repetition are to be avoided), nor as to the number of investigators who may work together. No preference will be shown to one nationality over another, nor to members of any particular Institute, nor to manuscripts in English over those in another

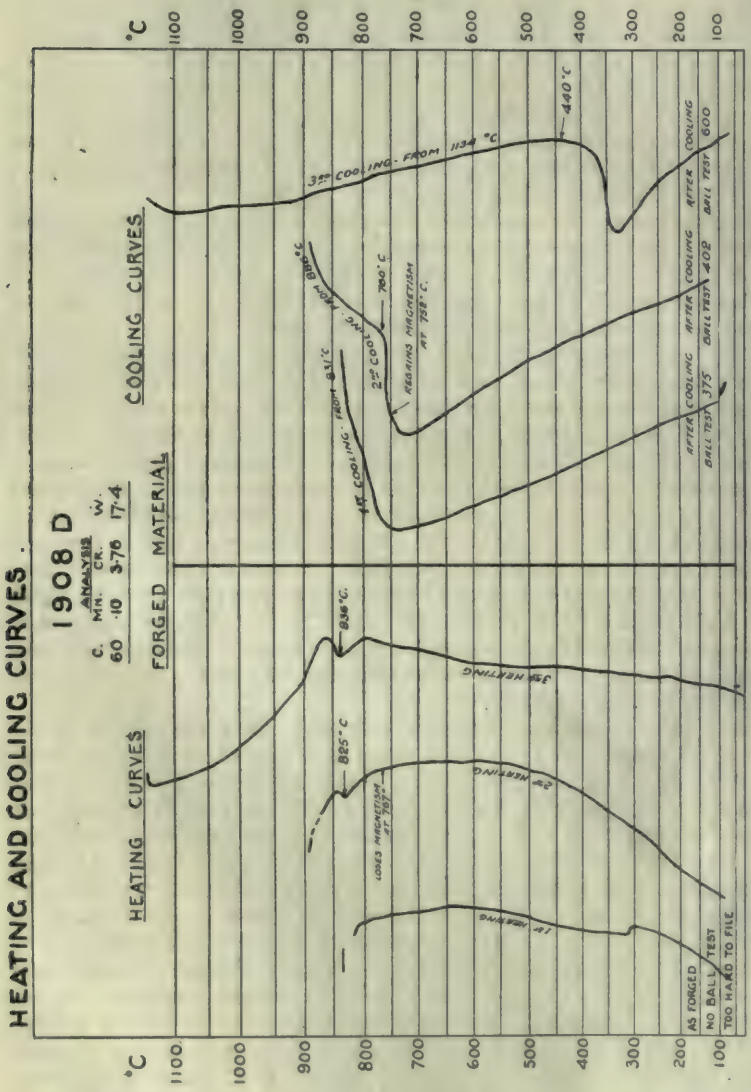


FIG. 1.

language. They will be all judged upon their merits and upon the same terms. It is desirable that all manuscripts should be typewritten.

In order to facilitate the researches, every reasonable assistance will be given by the Institutes concerned in making available the results of previous researches upon this and allied subjects; in fact, a bibliography of the subject will shortly be published in the *Bulletin* of the American Institute of Mining

Engineers, and a copy of this will on application be furnished gratis to those who expect to compete for the prize. As far as possible this Institute has also been good enough to offer to loan copies of rare publications from its Library, and these loans will be made strictly in order of application and for a limited time only. Moreover, in addition to these free services, there are special services which the Library is accustomed to render to its members and non-members for a moderate fee, which might prove helpful to competitors. These include making abstracts, special bibliographies, translations, photoprint copies, etc.*

Special Alloy Steels.

Turning now to the question of research work carried out in connection with alloys of iron with other elements, in order to show the small amount of attention devoted to alloy steels by Crookes and Röhrig, this now so vastly important side of metallurgy was disposed of in only a few pages, under the heading of "The Influence of Foreign Mixtures on the Proportions of Steel."

In Kohn's book, which, as stated above, I have taken as my starting-point, I can only find amongst its 270 pages one reference to a paper on the subject of special alloy steels with which I am dealing, namely, by Mr. Thomas E. Vickers "On the Strength of Steel containing Different Proportions of Carbon." This I have always looked upon as being one of the first papers that attempted to deal with the varying influence which a metal, or a metalloid, has upon iron. It was written in 1863 by Mr. Vickers, who, happily, is still with us. We are deeply indebted to him for his very important observations, as this paper was one of the forerunners in the development of this important branch of metallurgy from which the world to-day is deriving so much benefit.

Effect of Carbon upon Iron.

In the matter of alloys of iron with other elements, the fact should not be lost sight of that carbon still pre-eminently holds a position of supreme importance, for the presence of carbon even in special alloy steels is, with some few exceptions, absolutely necessary. Take as an illustration high-speed tool steel, which has led to such an enormous saving in machine-shop practice, with consequent benefit both as regards quicker and greater output, combined with greater precision of execution. Whilst the carbon present need not be relatively high, yet there must be sufficient carbon present otherwise the cutting properties of the steel in question would not be attained. The explanation is probably as follows: In high-speed tool steel of modern composition there is usually about 16 to 20 per cent. of tungsten, 2 to 4 per cent. of chromium, and about ·70 per cent. of carbon. Before treatment of the steel, the carbon exists in the form of carbide carbon and hardening carbon as defined by Ledebur.

Hardening carbon	·18 per cent.
Carbide carbon	·56 „
Total carbon	·74 „

After treatment, and with the nose of the tool in the condition required for mechanical work, we find the carbon content to have been transformed into

Hardening carbon	·60 per cent.
Carbide carbon	·14 „
Total carbon	·74 „

* A valuable contribution to this subject has been recently made by Dr. J. O. Arnold, F.R.S., and Mr. A. A. Read, M.Met., in their research read before the Institution of Mechanical Engineers, entitled "The Chemical and Mechanical Relations of Iron, Tungsten, and Carbon, and of Iron, Nickel, and Carbon." Also a remarkable paper, entitled "The Chemical Relations of Carbon and Iron," read before the Chemical Society in 1894.

Therefore, when we talk about the wonderful effect of the addition of elements other than carbon to iron, we must not fail to recognize that many, if not all, the new properties acquired by the steel are due entirely to the marvellous change that the treatment has wrought in the form of the carbon present, that is, its transformation from the soft or carbide carbon into what is believed to be the hardening or hardenite form of carbon, that is, the alloy

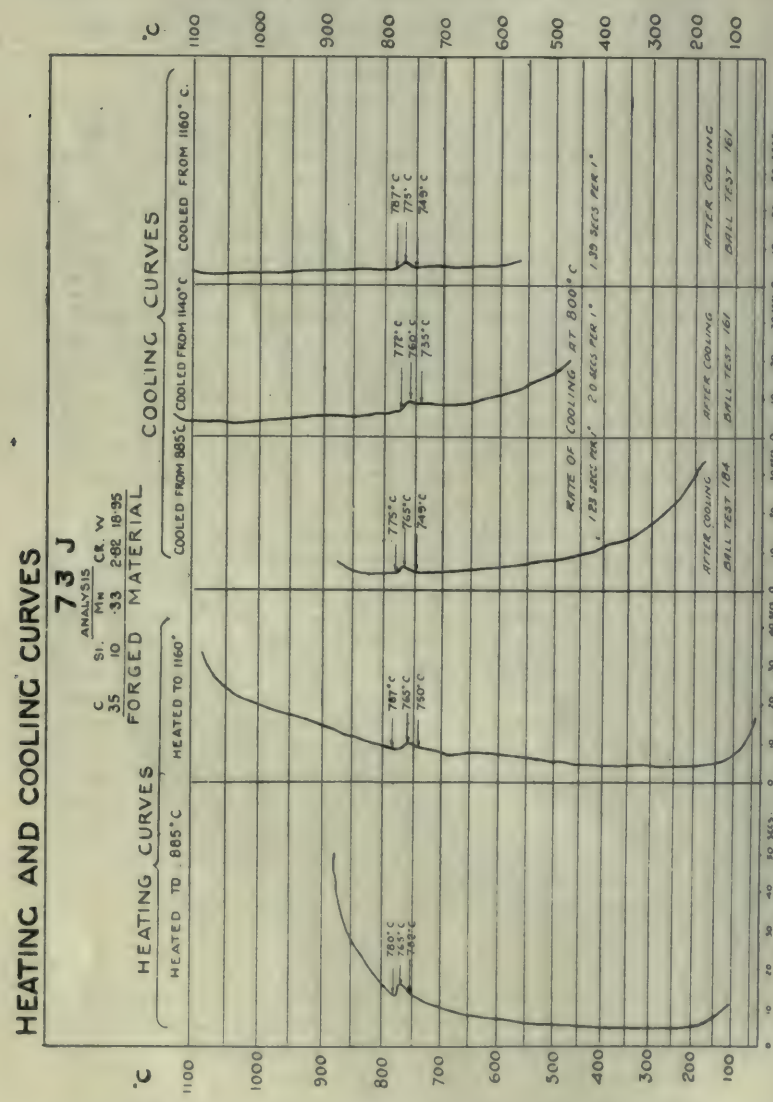


FIG. 2.

elements which enable the hardening carbon—or call it what you will—to retain its hard cutting properties in the steel. Whilst a similar change occurs by heat treating any low-carbon steel, that is to say, carbon steel without other modifying elements present, or present in very small percentages only, the chromium and tungsten in high-speed alloy steel maintain, or assist in maintaining, the hardenite present in that form, so that the cutting edge

TABLE II.—*Tensile Tests.*

No. of Test Bar.	Forging or Casting.	Machined or Forged.	Taken from	Transverse or Longitudinal.	Pattern.	Treatment.	Permanent Set.	Breaking Load.	Elongation. Per Cent.	Reduction in Area. Per Cent.	Ball Test.
6517F	Forging	Machined	Bar 1 in. sq.	Longitudinal	No. 2	Annealed.	11 Extensometer	52	14·5	18·64	255
5563F	Forging	Machined	Bar 1 in. sq.	Longitudinal	Brayshaw 2 in. × ·564	Air hardened at white heat	46·5 Extensometer	69·2	nil	nil	627

TABLE III.—*Static Fremont Test.*

No. of Test Bar.	Forging or Casting.	Machined or Forged.	Taken from	Transverse or Longitudinal.	Pattern.	Treatment.	Maximum Load. Kilos.	Energy Static. Kgm.	Angle.
6699F	Forging	Machined	Bar 1 in. sq.	Longitudinal	10 × 8 × 30 mm.	Annealed	2,100	0·18	3°

TABLE IV.—*Compression Tests.*

No. of Test Bar.	Forging or Casting.	Machined or Forged.	Taken from	Transverse or Longitudinal.	Pattern.	Treatment.	Elastic Limit.				Ball Test.
							·25 per Cent. set. Tons.	2½ per Cent. set. Tons.	5 per Cent. set. Tons.	Total set. Per Cent.	
5695F	Forging	Machined	Bar 1 in. sq.	Longitudinal	·7 × ·564	Annealed	18	53	61	25·7	235
5194F	Forging	Machined	Bar 1 in. sq.	Longitudinal	·7 × ·564	Air hardened at white heat	135	over 200	over 200	·143 Crushed at 284 tons per sq. in.	—

does not lose its hardness even when quite a considerable degree of heat caused by frictional contact is reached, which would entirely soften ordinary carbon steel.

The Author's Experiments on Alloy Tool Steel.

These remarks are based on experiments which I carried out as far back as 1903 with two grades of steel. The results of these experiments have not until now been published, so attention is specially drawn to them for the reason that they illustrate the very great importance of the metalloid carbon.

One of the alloys experimented upon had the following composition :

C.	Si.	S.	P.	Mn.	Cr.	W.
·74	·10	·04	·03	·28	2·84	18·00

The physical characteristics of this material (No. 73) were as shown in Tables II, III, and IV. It was tested in two conditions, (*a*) annealed, (*b*) air hardened at white heat.

The heating and cooling curves represented by Fig. 1 were taken upon steel No. 1908D. The qualities of the two materials are similar, the Carbon percentage in No. 73 steel being ·74 per cent., and in No. 1908D steel ·60 per cent.

Fig. 2 represents heating and cooling curves of steel No. 73J containing lower Carbon.

As regards the electrical qualities of this material, these are as follows. The permeability and retentivity or coercivity were determined by the Electrical Department of the Hecla Works Laboratory.

Tests were carried out on the steel No. 1908D, the following results being obtained :

TABLE V.

Treatment.	Electrical Resistance. Microhms per c.c.
"As forged"	40·79
775° furnace	31·37
1,200° air	56·53

Magnetic tests on the same material are shown in Figs. 3, 4, 5.

It will be seen from the heating and cooling diagrams that the magnetism probably disappears at a temperature of about 800° C. on heating and reappears at 750° to 735° C. on cooling—that is, in the Ar $_{1-2-3}$ point.

Tool Steel of Lower Carbon Percentage.

With a view to ascertain the effect of a lower percentage of carbon upon the alloy, the steel marked No. 73J was also prepared, having the following composition :

Mark.	C.	Si.	S.	P.	Mn.	Cr.	W.
73^{J}	·35	·10	·03	·03	·33	2·82	18·95

It will be observed that this steel, containing ·35 per cent. of carbon, was thus of the same composition as regards the "determining" elements, that is

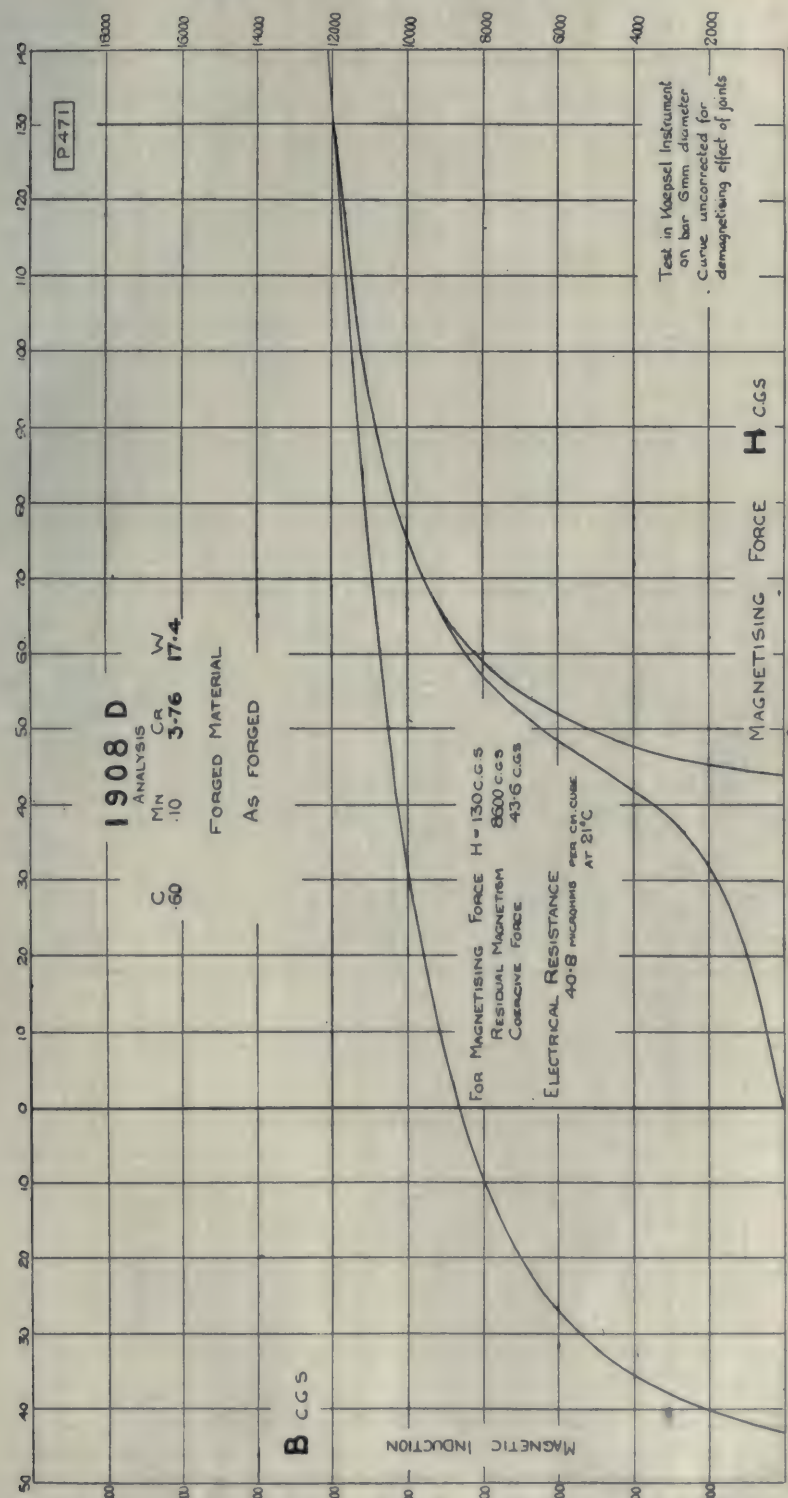

P471
1908 D
Analysis
C .60
Mn .10
Cr 3·76
W 17·4
Forged Material
As Forged
For Magnetising Force H = 130 C.G.S
Residual Magnetism 8500 C.G.S
Coercive Force 43·6 C.G.S
Electrical Resistance
40·8 microhms per cm. cube
at 21°C
Test in Koepsel Instrument
on bar 6mm. diameter
Curve uncorrected for
demagnetising effect of joints
B C.G.S
Magnetic Induction
Magnetising Force H C.G.S

FIG. 3.

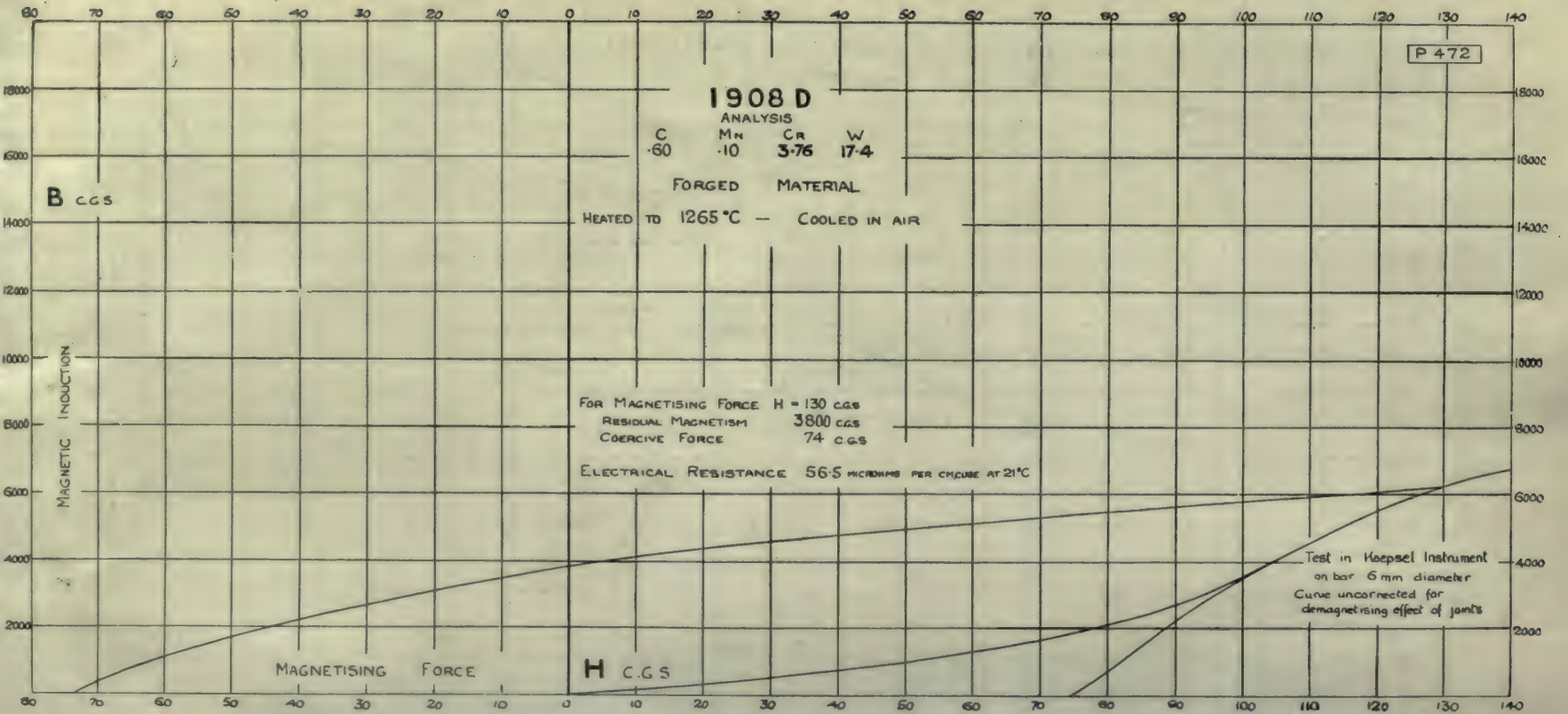

P 472
1908 D
ANALYSIS
C Mn Cr W
·60 ·10 3·76 17·4
FORGED MATERIAL
HEATED TO 1265 °C — COOLED IN AIR
B C.G.S
MAGNETIC INDUCTION
FOR MAGNETISING FORCE H = 130 C.G.S
RESIDUAL MAGNETISM 3800 C.G.S
COERCIVE FORCE 74 C.G.S
ELECTRICAL RESISTANCE 56·5 MICROHMS PER CM.CUBE AT 21°C
Test in Keepsel Instrument
on bar 6 mm diameter
Curve uncorrected for
demagnetising effect of joints
MAGNETISING FORCE
H C.G.S

FIG. 4.

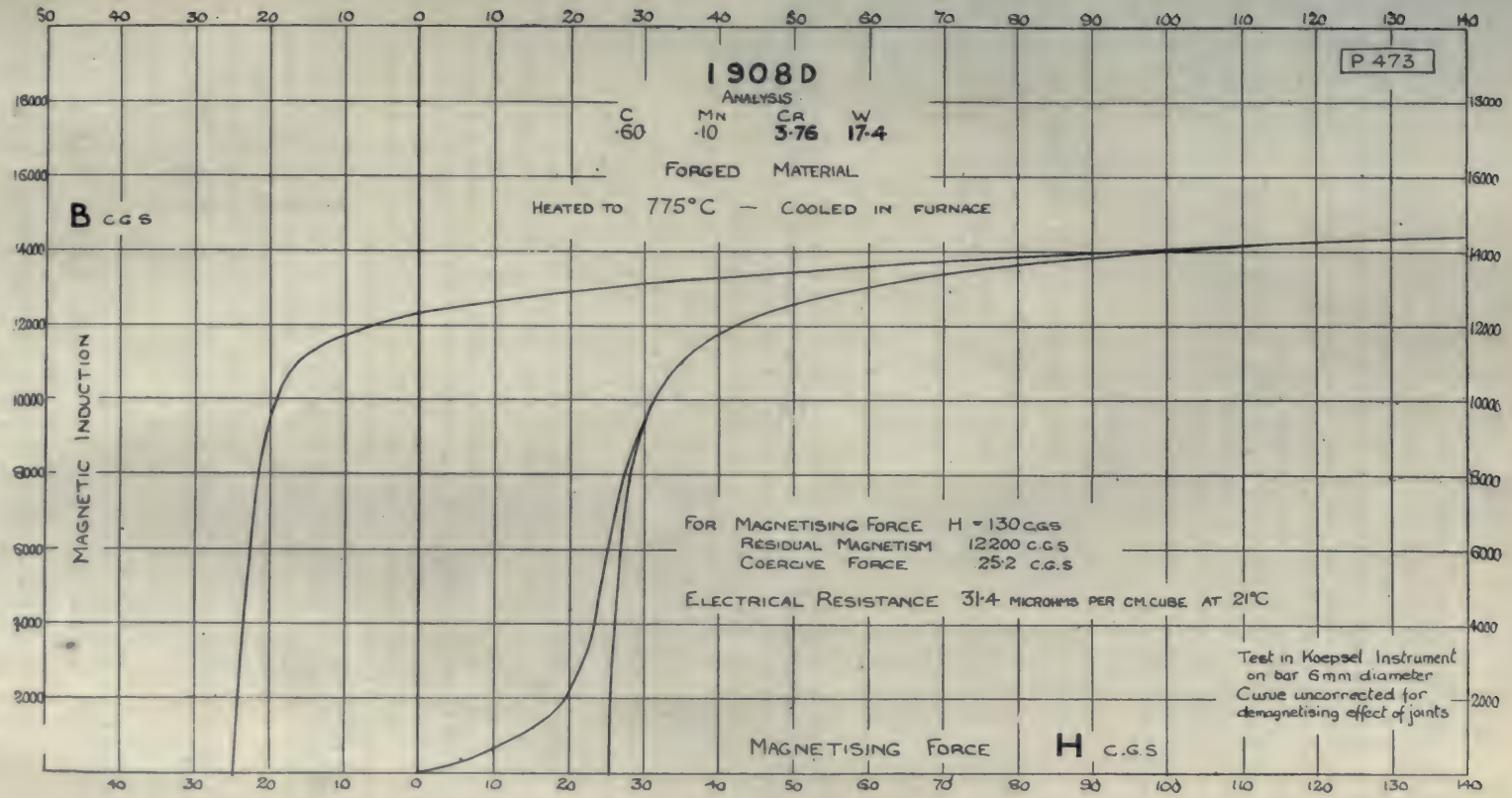

1908D
ANALYSIS
C .60
Mn .10
Cr 3.76
W 17.4
FORGED MATERIAL
HEATED TO 775°C — COOLED IN FURNACE
P 473
B C.G.S
MAGNETIC INDUCTION
FOR MAGNETISING FORCE H = 130 C.G.S
RESIDUAL MAGNETISM 12200 C.G.S
COERCIVE FORCE 25·2 C.G.S
ELECTRICAL RESISTANCE 31·4 MICROHMS PER CM. CUBE AT 21°C
Test in Koepsel Instrument on bar 6mm diameter
Curve uncorrected for demagnetising effect of joints
MAGNETISING FORCE H C.G.S

FIG. 5.

to say, those elements which are known as the special elements entering in the composition of high-speed tool steels, but the carbon percentage, say, about half. It was heat-treated in a similar manner to that carried out upon the specimen marked No. 73. It was, however, found to be quite useless for tools, being soft, and would not carry any cutting edge. There was practically no hardenite or hardening carbon present in this steel; the carbon was almost entirely in the form of carbide carbon.

On the other hand, the steel No. 73, after heating to about 1,100° C. and cooling in air, was found to contain no less than ·60 per cent. of hardenite, or hardening carbon, a circumstance which fully explains its valuable cutting properties. The following table, which refers to this steel No. 73, will be found interesting:

TABLE VI.

Mark.	Before Treatment.		After Treatment.		Ball Hardness.	
	Carbide Carbon.	Hardening Carbon.	Carbide Carbon.	Hardening Carbon.	Before Treatment.	After Treatment.
73	·56	·18	·14	·60	255	565/760

It will be seen from the curves in Fig. 2 that this material cannot be properly self-hardened. This is very remarkable in view of the fact that it contains nearly 19 per cent. of tungsten and nearly 3 per cent. of chromium, that is, nearly 22 per cent. of special elements, leaving only 78 per cent. of iron. The reduction from about ·70 per cent. carbon to ·35 per cent. has made it impossible for the material to become hard.

It will be noticed that this steel, No. 73J, containing ·35 per cent. carbon, possesses in the forged condition a ball hardness of 202; after cooling from 885° C. its hardness is 184; after cooling from 1,140°, also 1,160° C., its hardness is 161; in other words, there is no increase in hardness.

We have thus in the above a very clear proof of the correct value and action of carbon. From this it will be seen that the same element, carbon, which is so important in carbon steels and in other special steels, is of equal importance to the modern high-speed tool steels. If you leave out carbon from the latter the material is practically useless for the purpose in view. There could not be a stronger evidence of the importance of this element carbon, acting as it does in the presence of no less than three other important constituents, namely, manganese, chromium, and tungsten.

As will have been noticed, the second specimen, steel No. 73J, contained high percentages of chromium and tungsten, nearly 22 per cent. of these two elements together (2·83 and 18·95 per cent. respectively), but the carbon content had been reduced to ·35 per cent. This percentage of carbon in itself may be considered fairly high, and one might have expected that under the influence of the high percentages of chromium and tungsten present there would have been some hardening effect upon a tool made from steel of such a composition. When cooled in an air blast from white heat (this treatment being the same as that carried out upon the specimen No. 73), also quenched in water from a bright red or a white heat, the tool made of the steel No. 73J in each case remained quite soft. This illustrates in a marvellous way, as I have said, the influence of carbon. In other words, the effect of this lower percentage of carbon, as compared with the proper percentage for high-speed

TABLE VII.

Tensile Tests.

No. of Test Bar.	Forging or Casting.	Machined or Forged.	Taken from	Transverse or Longitudinal.	Pattern.	Treatment.	Permanent Set.	Extension at Permanent Set.	Breaking Load.	Elongation. Per Cent.	Reduction in Area. Per Cent.
6516F	Forging	Machined	Bar 1⅛ in. dia.	Longitudinal	No. 2	1,100° Air, 810° Furnace.	22	·002	49	·20	33½

TABLE VIII.

Fremont Tests.

No. of Test Bar.	Forging or Casting.	Machined or Forged.	Prepared from	Transverse or Longitudinal.	Pattern.	Treatment.	Nick Test.		Ball Test.
							"C" Nick.	No Nick.	
7725F	Forging	Machined	Test Bar 6516F 1⅛ in. diam.	Longitudinal	10 × 8 × 30 mm.	1,100° Air, 810° Furnace.	2 × 3°	20 × 45°	196
A5195 A5196	Forging	Machined	Bar 1⅛ in. sq.	Longitudinal	10 × 8 × 30 mm.	725° Furnace.	2·5 × 2°	8 × 22°	217

tool steel, is much the same at this low figure as the effect that would be obtained were there no chromium or tungsten present. After quenching there was no hardening carbon or hardenite formed. On the other hand, by increasing the carbon to the not very high point of ·74 per cent. (specimen No. 73), then the remarkable properties of high-speed tool steel were obtained.

The physical characteristics of the steel No. 73J were as shown in Tables VII and VIII.

This steel No. 73J showed an extremely fine crystalline fracture, about 20 per cent. being finely granular. The ball hardness of about 217 was obtained whether in its original condition (725° C. furnace) or in its heat-treated condition (heated to about 1,100° C., cooled in air, then reheated to 810° C. and cooled slowly in furnace).

I have specially devoted considerable attention to this particular steel because it illustrates in a clear and decisive manner the very great importance of the influence of carbon in determining hardness.

The work carried out by Abel, Müller, Arnold, and others with regard to the forms of carbon existing in steel created a great impression upon me, and it is largely their conclusions which have made me a carbonist rather than an allotropist.

The Great Work of Ledebur.

The late lamented Dr. A. Ledebur, of Freiburg, cast more light upon this dark place in metallurgy, namely, the relationship of iron and carbon, than

TABLE IX.

List of Papers by Dr. A. Ledebur relating to Iron and Carbon.

Title.	Source.	Date.
Some New Experiments and Theories on the Various Forms of Carbon observed in Iron and Steel	*Stahl und Eisen*	June, 1886
On the Nomenclature of the Various Forms of Carbon occurring in Iron	Ibid.	June, 1888
Sur la Denomination des Differentes Formes du Carbone dans les Fers Carbures	*Revue de Métallurgie*	Sept., 1893
Nouvelles Recherches sur la Teneur en Carbone des Fers Carbures	Ibid.	Sept., 1893
On the Processes Enacted in the Hardening of Steel	*Stahl und Eisen*	Oct., 1895
Various Forms of Carbon and Hardening of Steel	Ibid.	June, 1897
Manual of the Metallurgy of Iron (4th Revised Edition, First Part)	—	—
Annealing and Change in the Forms of Carbon by Heating	Reprint from *Stahl und Eisen*, No. 15	1897
Cementation Process	*Stahl und Eisen*	1906
On the Modifications of Carbon in Iron	Iron and Steel Institute	—
On the Forms of Iron and Carbon present in Malleable Iron, Steel and White Pig Iron	—	—
Determination of Carbide Carbon ...	*Guide Book for Steel Works Laboratories*	—

any one with whom I have been acquainted. So important do I consider this work that I give a list of his papers in case reference is desired to be made by any of those who feel interested in the subject, specially as some of them are not well known.

Allotropic Theory.

As you are all aware, bearing in view the papers quite recently read before the Iron and Steel Institute, it appears to me to have now been clearly proved that, as strongly indicated by my own earlier work many years ago and by that of other experimentalists, including those to whom I have just referred, there is no such form of iron as an adamantine "beta" form. It is important that this should be made widely known, because now the allotropic theory has been shown to be untenable, more attention will be devoted to other research—for example, in the direction of more fully determining the part played by carbon in that marvellous transition of the steel in its present extreme softness to great hardness—that is, from, say, about 100 Brinell ball number to 600, 700, or even 800, met with when we heat high carbon or other suitable steel to a sufficient degree and water-quench or otherwise suddenly or quickly cool it.

The Author's Papers on Alloys of Iron.

The subject of steel alloys is such an important one in all its bearings that I thought it might be found interesting, and also useful for reference purposes, to trace back some of the work done in this connection as indicated by various research papers which I have had the pleasure of presenting to the metallurgical world from time to time during the last twenty-five years. These papers give in chronological order the history of this particular branch of the metallurgy of iron and steel. In these papers, too, I trust full reference and credit has been given to the splendid work done by the scientists of all nations who have helped on the good work, whether in this country, America, France, Germany, Austria, Belgium, Sweden, or Spain. As before stated, not a little credit should be allotted to the early work of the Swedish scientists, for first separating for our use many of the elements which we are to-day using in our special steels. It is largely from their work we are to-day benefiting so greatly.

TABLE X.

Table showing in Chronological Order the Various Papers and Scientific Addresses by the Author of this Address, from the year 1888 *to the present time.*

No. and Title.	Name of Institute where Research was Read, or Press Reference.	Year of Publication.
1. Manganese Steel	Institution of Civil Engineers	1888
2. Some newly discovered Properties of Iron and Manganese	Ibid.	1888
3. On Manganese Steel... ...	Iron and Steel Institute	1888
4. Alloys of Iron and Silicon ...	Ibid.	1889
5. Alloys of Iron and Silicon (Abstract of Paper)	British Association	1889
6. Aluminium Steel	Iron and Steel Institute	1890
7. Alloys of Iron and Chromium	Ibid.	1892
8. Notes on the Chicago Exhibition	Ibid.	1893

No. and Title.	Name of Institute where Research was Read, or Press Reference.	Year of Publication.
9. Iron Alloys, with special reference to Manganese Steel	American Institute of Mining Engineers	1893
10. Huntsman, the Inventor of Crucible Steel	Ibid.	1893
11. Presidential Address ...	Sheffield Society of Engineers and Metallurgists	1893
12. The Early History of Crucible Steel	Iron and Steel Institute	1894
13. The Results of Heat Treatment on Manganese Steel and their bearing upon Carbon Steel	Ibid.	1894
14. The Production of Iron by a New Process	Ibid.	1895
15. Steel and Iron Alloys ...	Institution of Civil Engineers	1897
16. Foreign Technical Progress	Iron and Steel Institute	1897
17. Alloys of Iron and Nickel ...	Institution of Civil Engineers	1899
18. The Influence of Casting Temperature upon Steel	Ibid.	1899
19. Address as Master Cutler to the Cutlers' Company	Sheffield Press	1899
20. Address and Distribution of Prizes to Students at Technical Department of Sheffield University College	Ibid.	1899
21. On the Electrical Conductivity and Magnetic Permeability of Various Alloys of Iron*	Royal Dublin Society	1900
22. Researches on the Electrical Conductivity and Magnetic Properties of Upwards of One Hundred Different Alloys of Iron*	Institution of Electrical Engineers	1902
23. On the Magnetic Properties of an Extensive Series of Alloys of Iron*	Royal Dublin Society	1902
24. Alloys of Iron, Manganese, and Nickel	Institution of Civil Engineers	1903
25. Alloys of Iron and Tungsten	Iron and Steel Institute	1903
26. Iron and Steel Alloys ...	*Iron and Steel Metallurgist and Metallographist*	1904
27. Researches on the Physical Properties of an Extensive Series of Alloys of Iron*	Royal Dublin Society	1904
28. Magnetic Alloys from Non-Magnetic Metals	British Association	1904
29. Production of Magnetic Alloys from Non-Magnetic Metals	*Chemical News*	1904
30. On the Effect of Liquid Air Temperatures on the Mechanical and other Properties of Iron and its Alloys*	Royal Society	1904

* Joint paper with others.

No. and Title.	Name of Institute where Research was Read, or Press Reference.	Year of Publication.
31. Seventh Report of the Alloys Research Committee: On the Properties of a Series of Iron-Nickel-Manganese-Carbon Alloys *	Institution of Mechanical Engineers	1905
32. On the Magnetic Qualities of some Alloys not containing Iron *	Royal Society	1905
33. Presidential Address... ...	Iron and Steel Institute	1905
34. Experiments relating to the Effect of Mechanical and other Properties of Iron and its Alloys produced by Liquid Air Temperatures	Ibid.	1905
35. Effet de la Température de l'Air liquide sur les Propriétés mécaniques et autres du Fer et de ses Alliages	Congrès International des Mines, de la Métallurgie, de la Mécanique et de la Géologie Appliquée (Section de Métallurgie)	1905
36. "James Forrest" Lecture on Unsolved Problems in Metallurgy	Institution of Civil Engineers	1906
37. Presidential Address... ...	Iron and Steel Institute; Joint Meeting with American Institute of Mining Engineers	1906
38. Address to Students at Columbia University, New York	*Iron Age*	1907
39. The Magnetic Properties of Iron and its Alloys in Intense Fields *	Institution of Electrical Engineers	1910
40. A Research on the Hardening of Carbon and Low Tungsten Tool Steels *	Institution of Mechanical Engineers	1910
41. Expériences sur la Ségrégation dans les Lingots d'Acier	*Revue de Métallurgie*	1910
42. Address at Sheffield University on the Conferment of Honorary Degree of Doctor of Metallurgy (D.Met.)	Sheffield Press	1911
43. Sinhalese Iron and Steel of Ancient Origin	Royal Society	1911
44. Sinhalese Iron and Steel of Ancient Origin	Iron and Steel Institute	1912
45. Les Progrès de la Métallurgie	*Le Génie Civil*	1912
46. Abstract from Paper on Sinhalese Iron and Steel of Ancient Origin	*Nature*	1912
47. Abstract from Paper on Sinhalese Iron and Steel of Ancient Origin, with Addendum regarding Delhi Pillar	Royal Society	1912
48. Analysis of the Iron Pillar, made about 300 A.D., at Delhi	*Engineering*	1912

* Joint paper with others.

No. and Title.	Name of Institute where Research was Read, or Press Reference.	Year of Publication.
49. Contribution to the Discussion (International) on the Magnetic Properties of Alloys	Faraday Society	1912
50. The World's Progress in Metallurgy	*Iron Age*	1912
51. The Production of Sound Steel	Ibid.	1912
52. The World's Production of Pig Iron	*The Times*	1912
53. On a New Method of Revealing Segregation in Steel Ingots	Iron and Steel Institute	1912
54. Method of Producing Sound Ingots	Iron and Steel Institute	1912
55. Plant for Hadfield Method of Producing Sound Steel Ingots	American Institute of Mining Engineers	1913
56. Méthode pour Produire des Lingots d'Acier sains et Déceler la Ségrégation dans les Lingots d'Acier	*Revue de Métallurgie*	1913
57. Nouvelle Méthode pour Déceler la Ségrégation dans les Lingots d'Acier	Ibid.	1913
58. Heating and Cooling Curves of Manganese Steel	Iron and Steel Institute	1913
59. The Magnetic and Mechanical Properties of Manganese Steel	Ibid.	1914
60. Research with regard to the Non-magnetic and Magnetic Conditions of Manganese Steel	American Institute of Mining Engineers	1914
61. Sound Ingots	Ibid.	1914
62. Manganese Steel Rails	Ibid.	1914

In presenting this Table X, I regret in one sense that it covers only my own personal studies. During the early stages of this branch of metallurgy, and up to the time when commencing my researches about 1882, there were, however, practically no papers on record relating to this subject. It seemed to me, therefore, that this table showing my own research records and papers might prove of service to those interested, as these truly represent the leading lines of progress which have been made in this branch during the last thirty years, and also give in chronological order the progress made in this wonderful art of alloying various elements with the master metal of the world—IRON. Moreover, as no complete list of these papers has before been published, the one now presented may prove a useful bibliography to those interested.

It will be remembered that Coleridge says of the Ancient Mariner that :

"He was the first who ever burst
Into that silent sea,"

which describes the situation existing about the date above mentioned with regard to metallurgical knowledge in this particular branch, for our knowledge of iron alloys was then indeed "a silent sea." Whilst splendid work in other directions of metallurgical science had been done by such men as Percy, Bessemer, Mushet, Siemens, Martin, Thomas, Gilchrist, Abel, Jordan, and others, the only records I am aware of with regard to iron alloys were those representing the work of the little band of pioneers—Gautier, Euverte, and Pourcel, of Terre Noire. For some unaccountable reason, however, whilst they were on the threshold of this wonderfully fruitful field they stopped short and it was permitted to others to pass through the door.

Amongst other matters, the papers set forth in Table X deal with manganese steel and its most remarkable properties; with alloys of iron and silicon; iron and aluminium; iron and tungsten; iron and nickel; iron and chromium; also with a large number of other binary, ternary, and quaternary steels.

This address does not attempt to consider and deal with more than certain portions of thought with regard to the progress of metallurgy. Otherwise it would require not one paper of a few pages, but many books, so great has been the development on all sides of modern metallurgy. Our ancient friend before mentioned, Tubal Cain, or his confrères of the last century, would indeed be surprised with what he would now see in the advance of this branch of science.

In order to make the special subject of alloys of iron more clear, I may also add the following description in Table XI of some of the researches dealt with in my papers, from which will be seen the large number of alloys of iron and other elements which have been dealt with.

TABLE XI.

No.	Alloy.	No.	Alloy.
	Binary Alloys.		*Ternary Alloys.*
1	Carbon	16	Nickel-Manganese
2	Boron	17	Nickel-Chromium
3	Manganese	18	Nickel-Tungsten
4	Nickel	19	Nickel-Silicon
5	Copper	20	Nickel-Aluminium
6	Cobalt	21	Nickel-Molybdenum
7	Chromium		*Quaternary Alloys.*
8	Tungsten	22	Carbon-Nickel-Manganese
9	Molybdenum		*Quinternary Alloys.*
10	Vanadium	23	Carbon-Tungsten-Chromium-Vanadium
11	Silicon		
12	Aluminium		
13	Sulphur		
14	Phosphorus		
15	Arsenic		

The results obtained will be found in the various papers detailed in the foregoing table, No. X.

It must not be forgotten that, although the above table of alloys refers chiefly to the influence of one or more special elements upon iron, yet the qualities of such alloys are largely affected by the presence of what may be termed the leading element, carbon, which is usually also present. As I have shown in the present Address, although in the case of high-speed tool steel the carbon percentage is not high, its influence is literally enormous, for, as I

have shown, reduce the carbon below certain limits and you have a comparatively useless product.

Beyond a small number of exceptions—important ones, it is admitted; for example, the materials known as "ingot iron," "low hysteresis steel," and some others—all the known "steels," including even mild steel, largely depend for their properties upon the percentage of carbon present, and consequently for their commercial value.

Thermal Treatment.

Whilst there are still left elements to be alloyed with iron, and upon which there is ample field for investigation and research, we are, so to speak, nearing the top of the hill. It cannot be very long, unless new elements are discovered, which is not probable, before we shall be able to say that there is little or no more room for discovering new alloys or combinations, and that attention will then have to be turned still more closely than even now to the effect of thermal treatment. This may quite possibly imply treatment at lower grades of temperature than those which we now imply by the term "heat treatment," which leads me to make the following remarks.

Low Temperature Experiments in Great Britain and America.

The recent prosecution of research in the direction first dealt with by our great scientist, Sir James Dewar, that is, the behaviour of metals and their alloys at temperatures approaching absolute zero, shows that there is much to be learned from an examination of the physical properties and behaviour of metals and their alloys at such temperatures.

In the joint research carried out by Sir James Dewar and myself, a full description of which will be found in my paper on "Experiments relating to the Effect on Mechanical and other Properties of Iron and its Alloys produced by Liquid Air Temperatures," read before the Iron and Steel Institute in September, 1905, it was shown that great increase of tensile strength in steel alloys could be obtained; in one case a tensile strength of over 150 tons per square inch was obtained, not merely from a wire, but from a forged bar.

Recent experiments in America show that at a temperature of about minus 435° F., or close upon absolute zero, metals lose their resistance to such a remarkable degree that the energy developed at the power-house of Niagara, so it is stated, could be transmitted over a quite small metallic wire, simply because resistance vanishes at these temperatures. It will therefore be seen that there is good ground for my statement that before long we may have to consider not merely heat treatment effects, that is an increase over normal temperature, but also treatments below normal temperature.

Field for Research.

It will be seen that even to-day the field for research has been and still is an immense one; it is full of difficulties and perplexities. Contradictions often seem to present themselves. Nevertheless, the advance made in this branch of alloy steels since the date of my first researches in 1882 and onwards, also my paper on "Manganese Steel" in 1888, has been of a startling nature.

Whilst it is true there may not be at the present time room for such abnormal discoveries in ferrous metallurgy as in the past, yet workers all over the world are quietly and steadily adding to our stock of knowledge on points, some of which may not seem so important at the time, but all of which tend to enable us to better understand and therefore control the desired qualities of iron and its alloys.

Table XII.

Magnetic and Mechanical Tests upon Manganese Steel in its Non-magnetic and Magnetic Conditions, taken from Hadfield and Hopkinson's joint research.

Arranged in Three Groups:
"A"—Completely or Practically Non-magnetic (less than 1 per cent. Magnetism).
"B"—Partly Magnetic (1 per cent. to 12 per cent. Magnetism).
"C"—Very Magnetic (20 per cent. Magnetism and over).

Note 1.—Analysis of the Material—

C.	Si.	S.	P.	Mn.
1·21	·22	·030	·080	12·36 per cent.

Note 2.—"S.C.I." refers to Swedish Charcoal Iron of about 99·82 per cent. purity Fe.

Test Piece No.	Specific Magnetism. S.C.I. = 100.	Brinell Hardness Number.	Bending Test: ⅞ in. × ⅜ in. × 1½ in. between Supports. Corrected Load. Maximum in lb.	Bending Test: ⅞ in. × ⅜ in. × 1½ in. between Supports. Angle of Bend (Degrees).	Temperature in Degrees Centigrade.	Specimen Cooled Down in	Duration of Heat Treatment. Hours.
"A"—Completely or Practically Non-magnetic (less than 1 per cent. Magnetism).							
	·3	207		180 Unbroken		Quenched from yellow heat in water	No further treatment
5857	·3	215	10,750	161	300 310	Furnace	168
5970	·3	267	10,900	21	750	Air	1
5971	·3	277	12,180	29	750	Water	1
5973	·3	277	12,890	29	530	Furnace	15
					750	Water	1
5298	*·2	337	10,360	8	450	Furnace	6
5972	Mere trace	339	10,920	11	530	Furnace	15
					750	Air	1
5402	·2	340	12,900	12	400	Furnace	6
5296	*·2	408	10,080	2	650	Furnace	3
5303	*·2	418	9,747	2	650	Furnace	6
5403	·6	340	11,680	8	400	Furnace	12
"B"—Partly Magnetic (1 per cent. to 12 per cent. Magnetism).							
5873	1·25	217	10,630	124	300	Furnace	552
5856	1·0	317	14,400	26	300	Furnace	384
					400	Furnace	
5855	1·0	328	12,900	17	300	Furnace	384
					400	Furnace	
5400	1·0	364	11,400	6	400	Furnace	24
5389	1·2	361	10,770	4	450	Furnace	12
5399	2·0	387	9,700	2	400	Furnace	48
5373	2·2	387	9,250	3	450	Furnace	24
5374	7·0	418	8,270	2	450	Furnace	48
5749	*12·2	444	7,420	1	600	Furnace	3
"C"—Very Magnetic (20 per cent. Magnetism and over).							
5661	*19·8	418	8,476	1	600	Furnace	12
5748	20·0	418	8,478	1	550	Furnace	6
5750	*20·4	351	12,570	11	500	Furnace	6
5336	*24·4	375	11,130	5	600	Furnace	24
5658	*24·8	402	11,810	4	550	Furnace	12
5304	25·8	438	10,140	2	550	Furnace	24
5369	28·8	351	9,970	3	500	Furnace	12
5713	*29·8	430	10,270	2	600	Furnace	72
5327	*30·0	418	11,270	3	600	Furnace	48
5330	*31·4	495	8,037	1	550	Furnace	48
5338	34·4	444	7,890	1	500	Furnace	24
5337	*40·2	438	7,460	1	500	Furnace	48
5364	*42·0	444	8,200	nil	500	Furnace	600

* Repeat tests were carried out on these specimens, similar results being obtained.

The Non-magnetic and Magnetic Conditions of Manganese Steel.

As an example, amongst some of the many curious features met with in alloys of iron with other elements is their behaviour with regard to magnetic qualities. Manganese steel, whilst non-magnetic naturally, can be made magnetic. Some of the nickel-iron alloys are also non-magnetic. Owing therefore to the many interesting problems presented by the alloy known as manganese steel, Professor B. Hopkinson, F.R.S., and myself have for some time been carrying on a research as to the effect of heat treatment upon manganese steel. This was read at the recent meeting * of the Iron and Steel Institute. In the paper I read before the Iron and Steel Institute in 1894 on "The Results of Heat Treatment on Manganese Steel and their Bearing upon Carbon Steel," it was shown that by certain heat treatment manganese steel could be made magnetic, also that this quality could be reversed. That is to say, a bar of manganese steel which is non-magnetic, either in its brittle or tough condition, can by heat treatment be made magnetic ; in other words, its specific magnetism can be increased until it is about half that of Swedish charcoal iron. These experiments aroused a good deal of interest at the time, many of the leading metallurgists taking part in the discussion which arose upon the facts noticed. Experiments were carried out upon alloys of iron and nickel, and this also seemed to possess this reversible quality, only by quite other treatment. Increase of temperature renders manganese steel magnetic, but does not apparently affect the nickel-iron alloys, or at any rate to the same extent. Low temperature, that is, liquid air temperature, renders the nickel-iron alloys magnetic, but has not the slightest effect upon manganese steel. These are very curious facts.

Some confusion has arisen because this non-magnetic alloy of iron and nickel, containing about 22 per cent. of nickel, is, as just mentioned, rendered magnetic, that is, by considerably reducing its temperature—for example, by immersion in liquid air. By some unaccountable means, many scientists came to the conclusion that the non-magnetic manganese steel and non-magnetic nickel iron alloys possessed similar qualities. This is incorrect, because manganese steel entirely differs from the iron nickel alloys in the fact that it cannot be rendered magnetic by submitting it even to lower temperature than that of liquid air. In other words, manganese steel cannot be rendered magnetic by such treatment. The only way to make it magnetic is to carry out the heat treatment shown in my paper of 1894 just referred to.

The joint paper by Professor Hopkinson and myself very fully elaborates a number of interesting facts with regard to the specific magnetism of magnetic and practically non-magnetic manganese steel.

As, however, the whole question is so interesting, I submit the following tables, which represent briefly some of the joint work carried out. For more full details and explanation I would refer those interested to the paper itself.

In a general way, Table XII shows the magnetic and mechanical tests upon manganese steel in its non-magnetic and magnetic conditions. The results have been arranged in three groups :—

"A"—Completely or practically non-magnetic (less than 1 per cent. magnetism).
"B"—Partly magnetic (1 per cent. to 12 per cent. magnetism).
"C"—Very magnetic (20 per cent. magnetism and over).

* Two joint papers have been read this year (1914) on this subject by Professor Hopkinson and myself. One at the May meeting of the Iron and Steel Institute on "The Magnetic and Mechanical Properties of Manganese Steel," the other at the February meeting of the American Institute of Mining Engineers on "Research with regard to the Non-magnetic and Magnetic Conditions of Manganese Steel."

TABLE XIII.

Magnetic and Mechanical Tests upon Manganese Steel in its Non-magnetic and Magnetic Conditions.

Arranged according to Temperature.

Temperature in Degrees Centigrade.	Duration of Heat Treatment. Hours.	Specific Magnetism. S.C.I. = 100.	Brinell Hardness Number.
"A"—Completely or Practically Non-magnetic (less than 1 per cent. Magnetism).			
300	168	·3	215
400	6	·2	340
400	12	·6	340
450	6	·2	337
530 Furnace 750 Water	15 1	·3	277
530 Furnace 750 Water	15 1	trace	339
650	3	·2	408
650	6	·2	418
750	1	·3	277
750	1	3	277
"B"—Partly Magnetic (1 per cent. to 12 per cent. Magnetism).			
300	552	1·25	217
300	384	1·0	317
300	384	1·0	328
400	24	1·0	364
400	48	2·0	387
450	12	1·2	361
450	24	2·2	387
450	48	7·0	218
600	3	12·2	444
"C"—Very Magnetic (20 per cent. Magnetism and over).			
500	6	20·4	351
500	12	28·8	351
500	24	34·4	444
500	48	40·2	438
500	600	42·0	444
550	6	20·0	468
550	12	24·8	400
550	24	25·8	438
550	48	31·4	495
600	12	19·8	418
600	24	24·4	375
600	48	30·0	418
600	72	29·8	430

In Table XIII the same figures have been arranged according to temperatures.

It will be seen that whilst the specific magnetism of the material shown in groups "A" and "B," with the exception of the specimens in group "B" heated to 600° C. and the one specimen heated for 48 hours at 450° C., is very little, certain differences present themselves. The specimens in group "A" may be termed practically non-magnetic; in group "B" there is a tendency to increase; in group "C," representing treatment between the critical temperatures of about 500° to 600° C., the specific magnetism is quite considerable, varying from 20 to 42 per cent. as compared with Swedish charcoal iron of 99·82 per cent. purity, Fe taken as 100.

One interesting point which comes out very clearly is that with the increase in specific magnetism, specially in the more magnetic material, the Brinell ball hardness numbers are greatly increased, in fact nearly double as compared with the original hardness of manganese steel, which is about 200. As shown by the tables, it is quite possible to have a ball hardness number of even as high as 418, yet the material remains practically non-magnetic, only ·2 per cent. of specific magnetism, so that the allotropist, so it seems to me, cannot draw any support from this fact.

In the specimens possessing high percentages of specific magnetism, the hardness in some cases reached 495, but one of the specimens in group "C" shows a ball hardness number of 444, yet it possesses no less than 42 per cent. of specific magnetism. Glass scratching hardness requires about 600 and upwards Brinell hardness number.

The results of the interesting research work by Professor Pierre Weiss have shown that this quality of specific magnetism of the metals in the iron group or their alloys probably largely depends upon quite other factors than allotropic modifications of the elements present.

Melting Points.

Another example of attempts being made to widen our field of knowledge is the work of Dr. G. K. Burgess of the Bureau of Standards, Washington,

TABLE XIV.

Melting Points of Elements of Atomic Weight 48 to 59.

Metal.	Melting Point with Micropyrometer.	Purity.	Probable Melting Point of Pure Element.
Nickel	1452 * / 1449 †	99·83	1452 ± 3
Cobalt	1477 ± 2 / 1478 ± 1 ‡	99·95	1478 ± 5
Iron	1533 ± 1 § / 1528 †	99·98 ± ·01	1530 ± 5
Manganese ...	1255	97–98	1260 ± 20
Chromium ...	1520	98–99	1520 to > Fe.?
Vanadium ...	1720	97–98	1720 ± 30
Titanium	1794 ± 12	99·9 +	1795 ± 15

* Assumed value on platinum strip; also observed value on iridium strip.
† Crucible melts in electric furnace.
‡ Crucible melts in electric furnace; also on iridium strip with micropyrometer.
§ Five samples all agreeing to within 3°.

D.C., who is at present engaged with myself in a joint research regarding the melting-points of the various iron alloys I have produced. We are already greatly indebted to Dr. Burgess for the work he has done in connection with high temperatures, melting-points, and other kindred subjects. One of his latest researches has been to clear up once and for all the melting-points of what he terms the "refractory elements," chiefly those of atomic weight from 48 to 59. We now have for the first time fully recorded the following information, which I have taken from his paper on "Melting Points of the Refractory Elements—Elements of Atomic Weight from 48 to 59," detailed in the *Bulletin* of the Bureau of Standards, vol. 10, reprint No. 205.

Dr. Burgess and Mr. J. J. Crowe also read another interesting paper on "The Critical Ranges A2 and A3 of Pure Iron," at the meeting of the American Institute of Mining Engineers held in October of last year, which will largely help us to settle and co-ordinate the many apparent inconsistencies in past research work on this subject.

Microscopy.

In an address of this nature, mention can only be made briefly of the important branch of metallurgical research known as microscopy. At the time of Kohn's book very little was known. Sorby * had practically originated this line, but there were few who had the prophetic eye to foresee the importance this branch of investigation would reach.

As Professor W. C. Fearnsides, M.A., F.G.S., pointed out in a recent and able lecture upon Dr. Sorby's work, he was without doubt the first to originate metallography, or the study of the microstructure of iron and steel, as well as other metals. Sorby's earliest research work was in 1849, when he prepared the first rock "slice" ever made, and his first microscopical study of "igneous" rocks was presented in his great paper, read before the Geological Society of London on December 2, 1857. Showing the incredulity existing at the time as to the value of Sorby's work, Professor Fearnsides says :

"Smiled at by Professor Tinnant when about to begin the research, jeered at by his friend Leonard Horner (Vice-President of the Geological Society), who, at the meeting to which the results were presented, remarked from the chair that 'he had been a member of the Geological Society ever since its foundation, and during the whole of that time he did not remember any paper having been read which drew so largely on their credulity,' Sorby lived on to have those same results acknowledged and to be acclaimed by the geologists of all nations, assembled to celebrate the Centenary of the Foundation of the Geological Society of London, as the founder of modern petrology."

Sorby's first work on the microscopical study of metals was in 1863. In 1864 he lectured on this topic in Sheffield, later in the same year communicating his results to the Bath meeting of the British Association.

The writer of this address well remembers in 1886 taking some of his first specimens of manganese steel to Dr. Sorby, in order to ask his views with regard to the microstructure of this curious alloy of iron and manganese. Owing, however, to the comparatively imperfect methods of examination then prevailing, Dr. Sorby was not able to definitely report any special characteristics that would throw light upon this non-magnetic material with its many peculiar physical properties.

It was in 1885 that Dr. Sorby was first able to show the true composite

* Plate VII. is a photograph of the late Dr. Sorby, F.R.S., in his robes as Vice-Chancellor of the University of Sheffield.

PLATE VII.—THE LATE DR. SORBY, F.R.S.

nature of the "pearly constituent" of steel, as an aggregate of parallel plates. This discovery was the earliest recognition of the formation of crystals from a solid solution, and may be considered as the crowning achievement of his microscopical research. It was announced to the Iron and Steel Institute in 1886, and in 1897 in his paper on "The Microscopical Structure of Iron and Steel." Soon afterward, these discoveries appeared to be the signal "for great activity in the metallographic field, which he so brilliantly had started to explore."

It is not always possible to show who is the real originator and discoverer of lines of new thought. In this case, however, the pioneer's honour in leading the way in the study of the microstructure of metals is due to Dr. Sorby, and to him alone.

Happily, the mantle of Sorby as regards microscopy fell upon young and able shoulders in Sheffield, and Arnold, who has continued and greatly enlarged this important science, was for many years in close touch with the great master Sorby, of whom Sheffield is so proud.

Stead, Osmond, Sauveur, Heyn, and many others have assisted the good work. Kohn in his book devoted a couple of columns to the consideration of "Steel under the Microscope," but Dr. Percy, to whom we all owe a deep debt of gratitude, in his classic work of more than a thousand pages, *The Metallurgy of Iron and Steel*, published a little earlier than Kohn's work (1864), never even referred to this subject of the study of the microstructure of iron and steel! When we consider the army of microscopists of to-day working throughout the world in this branch alone of metallurgical work and research, preparing daily thousands of photomicrographs with a view to studying the proper structure of steel products for the guidance of both producer and user, it can well be understood why we have advanced so much in our general knowledge of the subject.

Dr. Percy's Work.

The work of Dr. Percy just referred to was indeed a classical one; even now one can obtain from it valuable knowledge and aid. His careful and well-prepared descriptions of plant, processes, and research are still of high value, and must have been specially appreciated when so little knowledge existed on the subjects he dealt with. It has been men such as Dr. Percy, who have spent their whole life in furthering the particular science with which they have identified themselves, who have conferred such large benefit upon the world. All honour to such men, whose only reward, the only one they ever really appreciated, was the satisfaction of knowing that they were following their calling to the best of their ability. Their labour was in the true sense a labour of love.

Dr. Percy devoted some consideration to the alloys of iron. His master mind, like that of Faraday forty years earlier, saw some of the possibilities of these combinations of iron with various elements. Unfortunately, Dr. Percy's alloy experiments were most of them on such a small laboratory scale, the product generally weighing at most a few ounces, that the results he obtained were naturally more of academic than of practical value. The whole of his observations with regard to what is probably the most important of the iron alloys, namely, iron and manganese, are summed up in a few lines: "We have already," he says, "considered carburized alloys of iron and manganese, but the presence of carbon, it need hardly be remarked, may be expected to modify the properties of any alloy in a material degree. With regard to alloys of pure iron and pure manganese, I do not know whether anything satisfactory has been published; I have not met with anything of the kind." This statement was indeed prophetic.

Naturally the highly carburized alloys of iron and manganese to which Dr. Percy referred were really spiegeleisen containing at the most 7 or 8 per cent. of manganese.

There were but few ferro alloys made before about 1865, and those which were produced contained high percentages of carbon, the presence of which completely altered the character of the product. This was the reason why the properties of that extraordinary alloy "manganese steel" were disguised and masked under the predominance of the carbon present in the manganiferous alloys formerly produced. Thus the production and manufacture of an alloy which has proved of such great advantage to mankind remained hidden for another twenty years. It was the study of this particular alloy, which I discovered about thirty years ago, which may be truly said to have been the first systematic study of alloys of iron with other elements. Mushet had made what was then termed self-hardening alloy steel, but its manufacture was shrouded in mystery and its application of comparatively small nature. Moreover its qualities were rather in the nature of a superior cast iron than steel.

"The Art of Scientific Discovery."

In the foregoing I have referred, but very briefly, to some of the research work carried out in one branch of science, ferrous metallurgy. This research question is one of the greatest importance, and covers an immense field. Gore has dealt generally with this in a most interesting and full manner in his remarkable book on *The Art of Scientific Discovery*, published some thirty years ago, which every one interested in research should read.

Gore pointed out that there are even amongst scientific investigators those who consider that methods of discovery are incommunicable. But, as he added, original scientific research is not an incommunicable subject : it is a natural process, and being such it must have laws according to which it operates. It is effected by means of our mental powers, and is therefore subject to the rules of mental action, and is communicable by ordinary natural methods. It is also being reduced as knowledge advances to rules of action, and will continue to be one of the noblest of all intellectual employments.

Why Research Work is so Valuable.

The value of research work is now generally recognized. A large portion of the admirable Presidential Address delivered by Sir H. Frederick Donaldson, K.C.B., in April last before the Institution of Mechanical Engineers was devoted to the consideration of this subject. That Institution has proposed to start a movement to co-ordinate research work so as to prevent the considerable amount of overlapping now existing. Whilst fully agreeing with this step, I believe that co-ordination in research work should not be made to interfere in any way with individual research ; many works dealing with metallurgy and engineering in all its branches have fully equipped laboratories for carrying out experiments in connection with their own manufacture, these experiments forming part, as it were, of their ordinary routine work, and they have always been found ready to make known many of the important results at which they have arrived. A simple glance at the list of contents of any one of the TRANSACTIONS of our Society, amongst other societies and institutions, suffices to show that metallurgists and engineers in this country cannot be taxed with working in secret ; and whilst agreeing in the main, as stated above, with the movement which Sir Frederick Donaldson would like to see initiated, individual effort, to my mind, should not and must not in the least be interfered with.

The Work of the National Physical Laboratory.

In this connection I should like to add that we have available for all kinds of researches and experiments a most admirable institution, the National Physical Laboratory, whose able Director, Dr. R. T. Glazebrook, is one of our esteemed Past-Presidents. The work of this institution bids fair to standardize many discoveries; it provides also a powerful aid to many individual experimentalists. To illustrate my point, it is sufficient to mention the investigations carried out in the Metallurgical Section and at the Froude tank at Teddington. It is no secret that if the experts at the Laboratory had sufficient funds at their disposal their investigations would have a much wider scope. At the present time they have on hand more than a hundred different investigations waiting to be taken up when the funds are available. The Laboratory is supported by grants made by the Government itself and various British scientific and technical institutions, who thus recognize its value; nay, the establishment itself of the Laboratory was largely due to the initiative of the institutions in question. It is a great national asset which, it would seem to me, the State should recognize to a greater degree than has been the case, and should grant it more substantial financial support out of the public funds.

Past Progress in Metallurgy.

In the foregoing I have alluded to the future exhaustion of our mineral resources and the necessity which is incumbent upon us for utilizing the metal iron, of which we have at best only the trusteeship, to a maximum degree. My present address, whilst it deals in the main with researches and discoveries in the matter of iron alloys, would be incomplete were I not to mention the marvellous inventions of Bessemer, Thomas, and Gilchrist, all Englishmen. These men in truth may be veritably styled benefactors of humanity, for they have largely increased the modern convenience and comfort of the world by making it possible to produce commercial steel at a comparatively low cost, therefore more cheaply, from what were considered inferior products before they put forward their processes of manufacture. On a par with these names are those of Siemens and Martin, who gave us the open-hearth process. The manifold advantages which the world has derived from the discoveries of these men would require more space than is at my disposal for their description. They are patent to all of us, and I am fully persuaded that future generations, whilst they may or may not give a passing remark to Tubal Cain as being the first metallurgist, will be sure to revere the memory of the above-named scientists, who by their researches accomplished so much, not only for the men of their own period, but also for their children's children. Future generations must surely, too, bear in mind those other scientists who have given to the world special steel alloys, remarkable among their other characteristic features by their wonderful toughness and tenacity, by their great durability and many other valuable qualities. They will further give also much more than a passing thought to that body of men of every nationality who are attacking the same problem from another side, the prevention of waste by corrosion, a matter to which our Society has given much attention.

The mere mention of these names and subjects opens to our minds an immense vista of consideration, actual realizations and future possibilities. I have here but touched the fringe, and will conclude with the following references and remarks.

The Scope of the University.

When His Majesty the King went to Manchester last July, Lord Morley as Chancellor presented to him an address from the University of that city. To this the King made answer saying: "It was to the Universities that the whole Empire looked for men equipped with scholarship and technical knowledge, and with will and energy to devote their gifts to the service of the community in every sphere of action." With this we must heartily agree.

A Degree congregation was held on July 3rd of last year at Sheffield University, under the presidency of the Chancellor, the Duke of Norfolk, when Mr. H. A. L. Fisher, the new Vice-Chancellor, uttered the following pregnant words: ". . . That University did not exist for the benefit of Sheffield; it was Sheffield's gift to the world. In such an important mining and metallurgical centre it was inevitable that these subjects—mining and metallurgy—should claim special attention, but the life of the mind brooked no territorial barriers, and discoveries made in the laboratories of that University would, no doubt, exercise a sensible influence in every quarter of the globe. They might be quite sure that no endowment lavished on research was ever lavished in vain, and that a wealthy community which devoted a part of its opulence to subsidizing clever men to think at large was discharging a manifest duty to the progress of the world."

The Faraday Society.

Faraday, Percy, and many other scientists, were among those men having "will and energy to devote their gifts to the service of the community," "clever men who thought at large," and our Society, by taking the name of the first, Faraday, has shown its earnest desire to continue in the footsteps of this great scientist. Our object is to promote the study of electrochemistry, electro-metallurgy, chemical physics, metallography and kindred subjects; our volumes of TRANSACTIONS give evidence of the "scholarship and technical knowledge" of our members, also, and this is a great point, of the international character of our work. Our programme is an extensive one, but from the very commencement we have tried to fulfil it in every respect. Our characteristic is the bringing together of the theoretical and practical sides of the problems we deal with, and having both considered and discussed by theoretical and practical men. Our membership, it is true, at present appears low when compared with the membership of other and older kindred Societies; but as I say, we have during these years fulfilled our programme, and we cannot but think that the work we have already done would receive the complete approval of our great master Faraday; we shall continue duly fulfilling this programme of ours in its entirety, and a time is sure to come when the work accomplished by the Faraday Society will also have its full share in the grateful remembrance of future generations.

Conclusion.

In conclusion, I feel that this address deals quite inadequately with the important subject which I have attempted to bring before your notice. If, however, it does nothing else than stimulate a desire for research in "the Art of Scientific Discovery," to use Gore's excellent term, then I shall indeed feel well repaid. Let us remember that "Labor improbus omnia

vincit." Thus as time goes on we shall acquire more and more knowledge in the great field of research.

As the poet Prince rightly says:

"Who are the great?
Those who have boldly ventured to explore
Unsounded seas, and lands unknown before;
Soared on the wings of science, wide and far,
Measured the sun, and weighed each distant star;
Pierced the dark depths of ocean and of earth,
And brought uncounted wonders into birth,
Repelled the pestilence, restrained the storm,
And given new beauty to the human form;
Wakened the voice of reason, and unfurled
The page of truthful knowledge to the world;
They who have toiled and studied for mankind,
Aroused the slumbering virtues of the mind,
Taught us a thousand blessings to create—
These are the nobly great."

Professor A. K. Huntington proposed a vote of thanks to the President for his Address. In the course of his remarks he said that the Faraday Society, which stood for the union between theory and practice, could have chosen no more suitable President than Sir Robert Hadfield, who was recognized both here and abroad as one of the greatest living exponents of the application of science to industry and industry to science. It was a source of pleasure to him, continued Professor Huntington, that it had fallen to his lot to persuade their new President to take office in succession to Dr. Glazebrook, but he was rewarded by the admirable Address they had just heard, which, sailing as they did under the name of "Faraday," in itself a most valuable asset, dealt with just those applications of science to industry which the members of the Society wanted to know about.

Mr. Alexander Siemens said it gave him much pleasure to second the vote of thanks to Sir Robert Hadfield. The President began his Address by speaking of the fascination of iron and steel; he had certainly succeeded in showing how fascinating the subject could become in suitable hands.

The Chairman then put the vote of thanks to the meeting. He said that Sir Robert Hadfield had spoken of the value of research. One had only to see Hadfield's Steel Foundry at Sheffield to realize the truth of this remark, and the Paper gave evidence of the value of his work. Sir Robert helped others to work too, and Dr. Glazebrook spoke of his generosity in supplying materials and assistance to other workers.

In the Address reference was made, in words which were greatly appreciated, to the work of the National Physical Laboratory. He took that opportunity on his part of saying how much they owed at the Laboratory to Sir Robert's support.

He was glad to have the privilege of putting the vote to the meeting. He did it with much pleasure, and in welcoming Sir Robert Hadfield he wished him a most successful year of office.

OPTICAL ROTATORY POWER.

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Friday, March 27, 1914, at the Chemical Society, Burlington House, London, W., a **General Discussion** on "**Optical Rotatory Power**" took place.

Professor H. E. Armstrong, F.R.S., presided during the afternoon session, and **Professor Percy F. Frankland, F.R.S.**, during the evening session.

Introductory Remarks of Professor H. E. Armstrong.

In the first place let me welcome the numerous visitors, especially our foreign colleagues. This Society, it is well known, has been exceptionally active in promoting general discussions of important subjects in chemistry and physics: that to be discussed to-day is one of outstanding interest from many points of view. The property possessed by certain liquids and solutions of rotating rays of plane polarized light was discovered and studied by Biot nearly a century ago; in the interval the views he put forward have been extended and applied chiefly by Pasteur, van't Hoff, Le Bel, etc.

This property is of special importance in relation to molecular and interatomic structure. It concerns even life itself, as the complex molecules met with in living material are optically active; what is most astounding, they all seem to be of some one type. It follows, therefore, that from the earliest period onwards there must have been a selective force in operation to produce one kind of material.

Two names stand out in particular in the early attempts to correlate the observations of optical rotatory power with molecular structure. The names I refer to are those of Crum Brown and of Guye, and I suggest it would be an act of grace if messages of greeting could be sent to these gentlemen from this meeting, so that they may realize how much their colleagues appreciate the service they have rendered in stimulating inquiry.

Another early worker was Sir W. H. Perkin, who did much to develop the spectroscopic method of observation as well as to extend the subject on the magnetic side.

It is gratifying that much of the early work has been done in this country, and that to-day we have the pleasure of welcoming Professor P. F. Frankland, Dr. T. S. Patterson, Professor A. Mackenzie, Dr. R. H. Pickard and Dr. T. M. Lowry, who have all made important contributions to the subject on the practical side.

For a long time, rotatory power was dealt with on narrow lines. The early workers used only monochromatic light of one wave-length. Much of the difficulty in interpreting the results is the outcome of this practice. We now recognize that the subject has to be put on a broader basis and at no distant date doubtless we shall be in a position to come to more definite conclusions than we have been able to do in the past, in consequence of the extension of the observations to lights of different degrees of refrangibility.

The papers to be read to-day are of considerable importance, especially that of Professor Tschugaeff, which is remarkable on account of the lucidity with which he presents his views.

Dr. Patterson, I notice, has much to urge against the term "anomalous rotatory dispersion." We must all agree that the term is not a happy one, but the great difficulty is to define what is normal. The only "normal" substances probably are the unsubstituted paraffins; as soon as we have to deal with unsaturated or with oxygenated substances, we introduce considerations which upset the normality. But I find some difficulty in understanding what Dr. Patterson's views are. He tells us "that the potentialities of the asymmetric carbon atom and of the most simple physical conception of those intermolecular forces to which liquefaction is due are ample to account for all the observed behaviour." * It appears to me that you cannot explain the complex phenomena met with by vague language of this kind, which seems to include everything. In the past, apparently, workers have dealt too much with substances such as the tartrates, which presumably can occur in more than one form; in the future, we must deal more with substances of known configuration which are not subject to change—if there be such—if we are to solve problems such as have been stated by Crum Brown and Guye and correlate rotatory power with structure.

* *Trans. Chem. Soc.*, 1913, **104**, 173.

THE INFLUENCE OF CERTAIN GROUPS ON ROTATORY POWER.

(TRANSLATED FROM THE GERMAN.)

Professor Dr. H. Rupe (Basle) read a Paper on "The Influence of Certain Groups on Rotatory Power."

My earlier experiments on the relation between constitution and optical activity were made with the menthyl esters of various acids; more recently, I have worked with derivatives of citronellal, of carvoxime, myrtenol, and methylene-camphor. One of my English colleagues has pointed out that we cannot expect clear answers to our questions except by using optically active compounds with only one asymmetric carbon atom, and that these must be liquid and give liquid compounds, so that no solvent is necessary.* But this is an ideal we are not able to attain in every case. Moreover, the same author has pointed out in a recent paper † that the influence of homologous groups on optical rotatory power is sometimes developed in a more striking way in solution than when no solvent is used. Again, whilst it is a most desirable thing to work with compounds containing only one asymmetric carbon atom, the influence on rotatory power of several asymmetric carbon atoms in one molecule is as yet very little understood. I have made a comparative table of corresponding series of compounds with one, two, and three asymmetric carbons, but have not been able to come to any conclusion about it, the material being as yet not sufficient. At the present time I am in agreement with Hilditch, when he says that the number of asymmetric atoms in a given molecule has little bearing upon the changes of rotatory power produced by constitutive influences. Here, indeed, we find a subject for future researches.

Influence of Alkyl Groups on Rotatory Power.

The change of rotatory power produced by the introduction of an alkyl group into a saturated or unsaturated chain (replacement of a hydrogen atom in $\cdot CH_3$, $:CH_2$ or $\vdots CH$) is usually insignificant; this was found to be the case, for instance, when a methyl group was introduced into the molecule of a saturated or unsaturated fatty acid, a phenylated acid, citronellal, carvoxime, or methylene-camphor. Several exceptions were indeed observed, but a special explanation can be given in almost every case. We are therefore entitled to state, as a general proposition, that the optical influence of saturated alkyl groups is a small one. ‡

* Pickard and Kenyon, *Trans. Chem. Soc.*, **99**, 45 (1911).

† Ibid., **103**, 1923 (1913).

‡ The branching of the carbon-chain of an alkyl group sometimes has a remarkable effect (Pickard and Kenyon, *Trans. Chem. Soc.*, **99**, 45 (1911); E. Fischer, *Ber.*, **42**, 2981).

Some authors* are of opinion that the accumulation of identical radicals upon a carbon atom near the asymmetric atom produces a kind of symmetry, which results in a diminution of rotatory power. I have studied this question with Ahner and wish now to draw your attention to the fact that, whilst the specific rotatory power of the substituted acetic esters diminishes a little from monomethyl- to trimethyl-acetic acid, the molecular rotatory power

TABLE I.

Menthyl-ester of	$[\alpha]_D$	M_D.
$CH_3 \cdot CH_2 \cdot COOH$	75·51	160·2
$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CH \cdot COOH$	72·05	163·5
$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CH \cdot COOH$	67·3	161·5

is practically constant. The symmetry of the trimethylacetic acid has therefore no marked influence on the asymmetric system (Table I).

Influence of Unsaturated Groups on Optical Rotatory Power.

Before dealing with this matter, I am glad to say that I agree in every point with Professor Frankland,† when he says: "The presence of unsaturation leads to an irregularity in the rotatory effect, and not necessarily to an increased rotation." To discover some law in these irregularities, to study those often contradictory facts, seems to me to be one of the most attractive problems of our science. It is well known that a double linking between two carbon atoms, in a position near the asymmetric carbon, has sometimes a powerful effect. If I am not mistaken, this was discovered by Walden.‡ In 1903 the great influence of Thiele's "conjugated" double bonds was discovered from experiments on the menthyl ester of sorbic acid, $CH_3 \cdot CH : CH \cdot CH : CH : CO_2R$.§ As time is too short to describe all the interesting researches that have been made in England on the influence of unsaturation on rotatory power, I will draw your attention exclusively to the effect of this conjugation.

Conjugation of Unsaturated Groups.

There are three different kinds of conjugation, which have all been well studied. I will begin with the simple conjugated double bonds between carbon atoms only, without any phenyl group. Data have been provided by the study of the menthyl-esters of sorbic acid and its reduction-products. In cinnamyl-acrylic acid we have, of course, a second conjugation with the

* *Zeitschr. f. physik. Chem.*, **77**, 482 (1911).
† Frankland, *Trans. Chem. Soc.*, **101**, 661 (1912).
‡ Walden, *Zeitschr. f. physik. Chem.*, **20**, 569 (1896).
§ Rupe, *Ann.*, **372**, 167 (1903).

phenyl group, but both vanish in phenyl-pentenic acid. But here we very soon meet with a curious fact, the anomaly represented by dimethylsorbic acid—

TABLE II.

	$[\alpha]_D$.
Menthyl-esters of Sorbic Acid and its Reduction-products.	
$CH_3 \cdot CH : CH \cdot CH : CH \cdot CO \cdot O \cdot C_{10}H_{19}$	88·53
$CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	65·11
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	64·86
*Menthyl-esters of Cinnamyl-acrylic Acid and its Reduction-products.**	
$C_6H_5 \cdot CH : CH \cdot CH : CH \cdot CO \cdot O \cdot C_{10}H_{19}$...	75·14
$C_6H_5 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	47·54
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	33·86
Menthyl-esters of Dimethylsorbic Acid and its Reduction-products.†	
$CH_3 \cdot C(CH_3) : CH \cdot C(CH_3) : CH \cdot CO \cdot O \cdot C_{10}H_{19}$	59·80
$CH_3 \cdot CH(CH_3) \cdot CH : C(CH_3) \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	68·51
$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	57·38

Looking for an explanation I was quite helpless for a couple of years, until Auwers and Eisenlohr discovered the very remarkable fact that the influence of conjugation on refraction is much disturbed by alkyl groups, connected with the double linkings, which may entirely destroy the optical exaltation which is observed in normal cases. There is a marked resemblance between Auwers' formulæ and that of the dimethylsorbic acid. In each case we have methyl groups, connected with the central carbons of the double bonds, exerting a powerful effect on the conjugation. I admit that this is no explanation, but at least we find here a remarkable analogy.

Frankland and O'Sullivan ‡ found that allyl and propyl derivatives frequently have the same optical rotatory power ; at least, the difference between the two is small, sometimes the former and sometimes the latter having the greater effect. I made the same observation in some experiments with Lenzinger § on the influence of the introduction of the allyl group in the menthyl esters of aceto-acetic acid and benzoyl-acetic acid. The rotatory

* Rupe and Münter, *Ann.*, **369**, 339 (1909).
† Rupe and Lotz, *Ann.*, **369**, 344 (1909).
‡ Frankland and O'Sullivan, *Trans. Chem. Soc.*, **99**, 2325 (1911).
§ Rupe and Lenzinger, *Ann.*, **395**, 135 (1912).

power of the menthyl ester was not at all remarkable, the unsaturated complex being too far away from the asymmetric carbon ; but when the double-bond of the allyl group is allowed to enter, in combination with a second one, so that a conjugation may be formed, we have again a strong optical effect. This rule is well demonstrated by the two compounds of citronellal, prepared by Jäger * from allylbromide and propylbromide in presence of magnesium. The conjugation here is nearer to the asymmetric carbon atom than in the above examples.

TABLE III.

	$[\alpha]_D$.	M_D.	
$CH_3 \cdot CO \cdot CH(CH_2 \cdot CH_2 \cdot CH_3) \cdot CO_2H$	57·27	161·6	Menthyl-esters of allyl- and propyl-derivatives of aceto-acetic and benzoyl-acetic acids.
$CH_3 \cdot CO \cdot CH(CH_2 \cdot CH : CH_2) \cdot CO_2H$	58·27	163·3	
$CH_3 \cdot CO \cdot CH(CH_2 \cdot CH : CH \cdot C_6H_5) \cdot CO_2H$	41·31	147·2	
$C_6H_5 \cdot CO \cdot CH(CH_2 \cdot CH_2 \cdot CH_3) \cdot CO_2H$	52·35	180·2	
$C_6H_5 \cdot CO \cdot CH(CH_2 \cdot CH : CH_2) \cdot CO_2H$	51·40	175·9	
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH_3$ ...	6·68	9·40	Derivates prepared from citronellal.
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH : CH \cdot CH : CH_2$ ...	10·12	18·03	

Influence of a Phenyl Group on Rotatory Power.

Very curious is the effect of a phenyl group and not easy to analyse. Close to the asymmetric carbon atom it nearly always increases the optical rotation. But here already we find some exceptions. Thus the benzoate of carvoxime † has a lower rotation than the phenylacetate and phenylpropionate. When the phenyl-group is displaced away from the asymmetric carbon atom, its positive increasing effect diminishes, until it becomes less than that of an alkyl-group. Finally, the effect may even become negative.

What is the reason of this phenomenon? There was a time when I thought that it might be the effect of a lever, that the influence of the phenyl group actually increased with its distance from the asymmetric carbon atom. I hoped to find Guye's well-known hypothesis in a new form. That may be correct, but it is necessary to be very cautious in this matter and to avoid drawing conclusions prematurely.

* Rupe and Jäger, *Ann.*, **402**, 149 (1913).

† Rupe and Wolfsleben, *Ann.*, **395**, 136 (1912).

TABLE IV.

	$[\alpha]_D$.	M_D.
$CH_3 \cdot CO \cdot O \cdot C_{10}H_{19}$	73·77	146·2
$C_6H_5 \cdot CO \cdot O \cdot C_{10}H_{19}$	90·90	236·5
$CH_3 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$...	75·51	160·2
$C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	67·57	185·0
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	70·46	159·6
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$...	58·48	186
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$ ...	64·86	164·9
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$ ...	33·86	107·0
Carvoxime $C_{10}H_{14}NO \cdot CO \cdot C_6H_5$	11·56	31·09
Carvoxime $C_{10}H_{14}NO \cdot CO \cdot CH_2 \cdot C_6H_5$	27·47	77·74
Carvoxime $C_{10}H_{14}NO \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_5$	77·23	77·90

Time does not permit me to give a full account of the work that has already been commenced in our laboratory, but here is a little contribution to this matter. When we compare the menthyl esters of the three acids: propionic acid, phenylacetic acid and hexahydrophenylacetic acid, the latter should have the greatest influence in diminishing the optical rotation, for there we have the heaviest mass at the end of the lever.

TABLE V.

	$[\alpha]_D$.
Menthyl-ester of propionic acid, $CH_3 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$ ...	— 75·51
Menthyl-ester of phenylacetic acid, $C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$ ...	— 67·57
Menthyl-ester of cyclohexylacetic acid, $C_6H_{11} \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	— 57·15

Experiments made in conjunction with Hoerder have shown that this is in fact what happens, the hexahydro-compound possessing the smallest rotatory power. But I will not insist on this fact, because the group C_6H_{11}, the radical of cyclohexane, has itself but little influence on the asymmetric carbon. In spite of its big mass and volume, its influence is not greater than the effect of an alkyl group, and is sometimes even smaller.

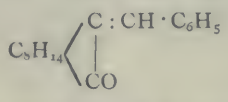
Specific and Molecular Rotation.

May I be allowed at this point to make a remark on specific and molecular rotation, which will, I feel sure, meet with some opposition? I agree that

molecular rotation is of the greatest value when we have to deal with homologous series (especially in aliphatic compounds). But when we replace, for instance, a methyl by a phenyl group, and thus pass from an inert alkyl group to an unsaturated group, with a large volume and much residual affinity, we should consider in the first place not the molecular rotation but the specific rotation; for if we think to eliminate the molecular weight by multiplying the specific rotation by the latter, we attribute too great an influence to this factor. Many subtle changes of constitution are indicated at once by variations of specific rotation where the molecular rotation leaves us in the lurch! *

Conjugation of the Phenyl Group with a Double Linking.

This combination has in every case a very marked influence on the optical rotation, especially when the conjugated group is close to the asymmetric atom. A few examples of the great amount of work done on this subject may be given. We have the interesting discoveries of Haller † in the camphor series, showing an enormous elevation of the rotation in benzylidene-camphor—



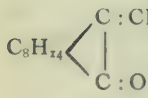
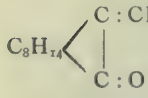
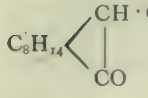
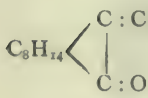
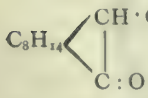
The rotatory power diminishes greatly when we exchange the phenyl group for the cyclohexyl-radical or the benzyl group, where we have no conjugation. Other examples are given (I) by the phenyl-derivative from citronellal and phenylmagnesiumbromide, ‡ by the corresponding cyclohexyl-compound, (II) by the hydrogen camphorates of eugenol and iso-eugenol, (III) discovered by Hilditch, § by cinnamylidenecamphor and phenylpropionyl-camphor, | (IV) by the optically-active esters of cinnamic acid and hydrocinnamic acid, ¶ (V) the diacetyl- and the dibenzoyl-ethyl-tartrate, ** (VI) the (above-mentioned) allyl- and propyl-derivative (VII) prepared by the reaction of allyl- and propyl-magnesium bromide with citronellal. ††

In his paper of the year 1909, ‡‡ on the effect of contiguous unsaturated groups on optical activity, Hilditch expresses the opinion that the influence of unsaturated groups depends at least as much on the proximity of the unsaturated nucleus to a carboxyl group as to the asymmetric system, or, in other words, on the degree of conjugation together with the nearness of the entire conjugated system to the asymmetric part of the molecule. Smiles, in his book of chemical constitution and physical properties, goes further when he quotes Hilditch, and says that the effect of unsaturated groups depends only on conjugation, and not at all on distance. On this point I am sorry to differ from my English colleagues!

More than ever, I am to-day of the opinion that the influence of a conjugation, or of any other group which largely increases or diminishes the rotatory power, is a function of its distance from the asymmetric carbon atom.

* Rupe, *Ann.*, **395**, 129 (1912).
† Haller, *Compt. rend.*, **136**, 1222 (1903).
‡ Rupe and Jäger, *Ann.*, **402**, 140 (1913).
§ Hilditch, *Trans. Chem. Soc.*, **97**, 223 (1910).
| Rupe and Frisell, *Ber.*, **38**, 104 (1905).
¶ Rupe and Busolt, *Ann.*, **369**, 356 (1909).
** Hilditch, *Trans. Chem. Soc.*, **99**, 224 (1911).
†† Rupe and Jäger, *Ann.*, **402**, 171 (1913).
‡‡ Hilditch, *Trans. Chem. Soc.*, **93**, I, 700, 1338, 1918 (1908); **95**, 289, 331, 1570, 1579 (1908); **97**, 223, 1091, 2110 (1910); **99**, 218, 224 (1911).

TABLE VI.

	$[\alpha]_D$.	M_D.
I		
	429·25	1020
	—	323
	—	248
II		
$C_6H_{11}\cdot CH(CH_3)\cdot CH:CH\cdot C_6H_5$...	63·24	135·4
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot C_6H_5$	7·62	
III		
$C_8H_{14}(CO_2H)\cdot CO_2\cdot C_6H_4\cdot CH:CH\cdot CH_3$ ...	38·6	
$C_8H_{14}(CO_2H)\cdot CO_2\cdot C_6H_4\cdot CH_2\cdot CH:CH_2$ ...	32·7	
IV		
	296·11	
	66·35	
V		
$C_6H_5\cdot CH:CH\cdot CO_2H$	76·95	220·8
$C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H$	58·48	168·4
VI		
$CH_3\cdot CO\cdot O\cdot CH\cdot CO_2C_2H_5$	—	9·9
$CH_3\cdot CO\cdot O\cdot CH\cdot CO_2C_2H_5$		
$C_6H_5\cdot CO\cdot O\cdot CH\cdot CO_2C_2H_5$	—	247·1
$C_6H_5\cdot CO\cdot O\cdot CH\cdot CO_2C_2H_5$		
VII		
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH:CH_2$ ...	10·12	18·03
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH_2\cdot CH_3$ ...	6·68	12·03

I am now working, with my assistant, on this subject. In a recent paper we were able to show that the phenyl-derivative, which Klages* prepared from citronellal and which we also studied,† has a strong exalting effect on the rotatory power, the conjugation being very near to the asymmetric atom. If now we displace the same conjugation a little further, the effect is marvellous! We see an extremely strong depression of the rotation.

TABLE VII.

	$[\alpha]_D$.	M_D.
$C_6H_{11} \cdot CH(CH_3) \cdot CH : CH \cdot C_6H_5$	63·24	135·4
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH : CH \cdot C_6H_5$	3·33	7·60

That the influence of a conjugation is a function of its distance from the asymmetric carbon atom is further demonstrated by the menthyl-esters of the α- and β-phenyl-cinnamic acid.‡

TABLE VIII.

	$[\alpha]_D$.	M_D.
$C_6H_5 \cdot CH : C(C_6H_5) \cdot CO_2H$	53·44	193·4
$C_6H_5 \cdot C(C_6H_5) : CH \cdot CO_2H$	37·92	137·4

Both acids contain a conjugation, but in the second acid this conjugation is remote from the asymmetric carbon atom.

It is Hilditch's§ merit that he directed attention to the influence of the carbonyl or ketonic group, which, as he proved, can very often enter into conjugation with an ethenoid group, thus producing an increased optical rotation. A very strong combination indeed is the benzene nucleus combined with the carbonyl-carboxyl group—$CO \cdot CO \cdot O$—and so forth. He regards the influence of the CO group as equivalent to the ethenoid group, or perhaps somewhat less; the combination of the carbonyl with the carboxyl group exerts an influence comparable to that displayed by a benzoyl radicle.‖

It may be useful to consider data for the derivates of menthyl acetoacetate and menthyl benzoylacetate.¶ Here also we see the very peculiar effect of distance (Table IX.); we remark how little is the influence of the various conjugations of the ketonic and the phenyl group. The conjugation of the phenyl group with the double linking is so far away from the asymmetric carbon atom that it has but little influence of the rotatory power.

* Klages and Santter, *Ber.*, **39**, 1939 (1906).
† Rupe and Jäger, *Ann.*, **402**, 179 (1913).
‡ Rupe and Busolt, *Ann.*, **369**, 311 (1909).
§ Hilditch, *Trans. Chem. Soc.*, **99**, 224 (1911).
‖ The strong influence of a $CO \cdot$ group has already been pointed out by Rupe and Frisell, *Ber.*, **38**, 106 (1905).
¶ Rupe and Lenzinger, *Ann.*, **395**, 87 (1912).

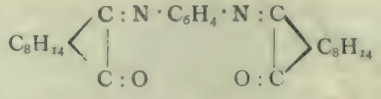
TABLE IX.

	$[\alpha]_D$.	M_D
$CH_3 \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_{10}H_{19}$ ...	70·50	169·3
$C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_{10}H_{19}$ ...	56·89	171·9
$CH_3 \cdot CO \cdot CH(CH_3) \cdot CO_2 \cdot C_{10}H_{19}$...	70·15	178·3
$C_6H_5 \cdot CO \cdot CH(CH_3) \cdot CO_2 \cdot C_{10}H_{19}$...	57·73	182 5
$CH_3 \cdot CO \cdot CH(C_6H_5) \cdot CO_2 \cdot C_{10}H_{19}$...	67·13	212·3
$C_6H_5 \cdot CO \cdot CH(C_6H_5) \cdot CO_2 \cdot C_{10}H_{19}$...	62·60	236·7

One can, of course, object that there is a possibility of an enolic structure $C_6H_5 \cdot C(OH) : CH \cdot CO_2 \cdot C_{10}H_{19}$ instead of a ketonic one. But in this second case we also find a conjugation, and measurements carried out by Lenzinger show that in alcoholic solution the change from the ketonic to the enolic form goes on very slowly, and the great uniformity of the figures suggests the same constitutional condition for all members of this series.

It is a rule that whenever the conjugation is destroyed, *e.g.* by reducing the double linking or the benzene nucleus, its strong influence on the rotation vanishes. But in the case of a distant conjugation which has produced little effect on the rotatory power, this destruction is of no importance.

Very remarkable is the enormous optical rotation of *p*-phenylene-*bis*-iminocamphor, pointed out by Forster and Thornley*—$[M]_D = 6100 [\alpha]_D = 1528$—a classical example of the effect of an uninterrupted chain of conjugations



between carbon, nitrogen, and oxygen atoms. Curious, too, is the great increase of the rotation which we observe when we double the molecule of menthyl-acetoacetate, that is, when we prepare the menthyl ester of diaceto-succinic acid.† Here the *molecular* rotation is doubtless of value, as we find $[M]_D = 398·6$, whilst the simple menthyl acetoacetate has $[M]_D = 134·5$. The first has a rotatory power almost three times stronger, and this fact is not so easy to explain, because there is no conjugation at all; but, remembering Knorr's wonderful work on this subject, the increased rotatory power may perhaps be attributed to the position of an enolic group:

$$\begin{array}{l} CH_3 \cdot CO \cdot CH \cdot COOC_{10}H_{19} \\ \quad\quad\quad\quad\quad\quad | \\ CH_3 \cdot C(OH) : C \cdot COOC_{10}H_{19}. \end{array}$$

The optical rotation of this well-crystallised compound increases rapidly when treated with piperidine in benzene solution; it rises from $[\alpha]_D$ 89·29 to

* Forster and Thornley, *Trans. Chem. Soc.*, **95**, 942 (1909).
† Rupe and Lenzinger, not yet published.

108·82°, reaching a maximum in the course of ten minutes. This further change is, perhaps, due to the formation of a second enolic group :

$$CH_3C(OH):C\cdot CO_2\cdot C_{10}H_{19}$$
$$\vert$$
$$CH_3C(OH):C\cdot CO_2\cdot C_{10}H_{19}.$$

Accumulation of Unsaturated Groups.

An unsaturated group has not always an exalting influence on the rotatory power, but very often produces the opposite effect. We nearly always observe a depression of the rotation when such a group is remote from the asymmetric carbon atom, but the same effect is often seen when it is near the active complex, especially when there happens to be, what I called in a paper published some years ago,* an accumulation of unsaturated groups, as, for instance, a benzene nucleus combined with a double linking, a conjugated double bond, a ketonic or a second phenyl-group.

A considerable amount of work has already been done on this subject. α- and β-phenylcinnamic acids both have a lower rotatory power than the corresponding saturated acids.† In the β-phenylcinnamic acid, where we find a heavy accumulation of unsaturated groups, we meet with one of the smallest rotations ever found in a menthyl ester. The corresponding saturated acid produces a much greater optical rotation. Moreover, we see, with one slight exception, that whenever a phenyl group enters an unsaturated chain, the specific rotation, and nearly always the molecular rotation, diminishes in comparison with the rotation produced by the corresponding methyl-compound.

TABLE X.

	$[\alpha]_D$.	M_D.	
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot C_6H_5$ ...	3·3	7·6	Hydrocarbons from citronellal. ‡
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH_3$ ...	6·6	11·0	
$C_9H_{14}O\cdot C:CH\cdot CH_2\cdot C_6H_5$	129·0	327·6	Derivatives of methylene-camphor.§
$C_9H_{14}\cdot O\cdot C:CH\cdot CH_2\cdot CH_3$	172·85	332·1	

In a recent paper by McKenzie and Martin ‖ there is a remarkable contribution to the effect on the rotatory power of an accumulation of unsaturated groups.

When we examine the effect of substituting a methyl for a phenyl group in the derivatives of acetic acid, we easily observe the depressing effect of the unsaturated nucleus, the diphenylacetic acid being a slight exception : but when we compare the corresponding esters of carvoxime the diphenylacetic acid is no longer exceptional. The very low rotatory power of the menthyl

* Rupe and Busolt, *Ann.*, **369**, 368 (1909).
† Ibid., *Ann.*, **369**, 356 (1909).
‡ Rupe and Jäger, *Ann.*, **402**, 140 (1913).
§ Rupe and Iselin, not yet published.
‖ McKenzie and Martin, *Trans. Chem. Soc.*, **103**, 112 (1913).

ester of triphenylacetic acid was found at the same time by Tschugaeff * and by my student Ahner.† Tschugaeff pointed out in his paper that this substance, which has an irregular rotatory dispersion, possesses an absorption

TABLE XI.

	$[\alpha]_D$.
$C_6H_5 \cdot CH \cdot (OH)CH_2 \cdot C(C_6H_5)_2 \cdot OH$	43·7
$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot C(CH_3)_2 \cdot OH$	72·3
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot C(C_6H_5)_2 \cdot OH$	138·0
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot C(CH_3)_2 \cdot OH$	67·6

band in the ultra-violet, which he regards as the source of the anomalous rotatory dispersion. That may be so, but it is only one example. In the last two years with my students I have measured the rotatory dispersions of

TABLE XII.

	$[\alpha]_D$.	M_D.
$C_6H_5 \cdot CH_2 \cdot CO \cdot OH$	67·57	185·1
$C_6H_5 \cdot (C_6H_5)_2CH \cdot CO \cdot OH$	66·70	226·8
$C_6H_5 \cdot (C_6H_5)_3C \cdot CO \cdot OH$	3·44	—

optically-active compounds with accumulations of unsaturated groups, and comparatively low rotations, but we have never found an anomalous one.

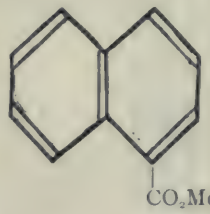
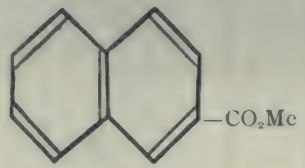
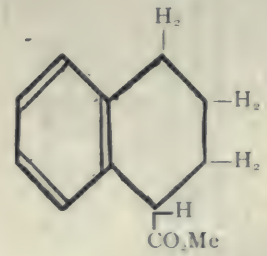
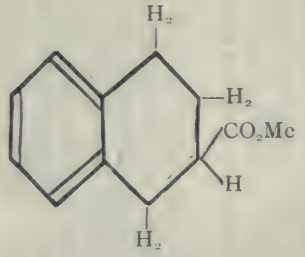
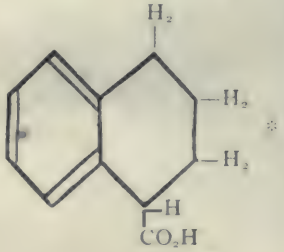
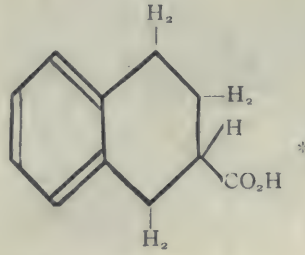
When we compare the menthyl esters of benzoic, *p*-methylbenzoic and *p*-phenylbenzoic acids, we find that the methylated derivative has the greatest and the phenylderivative the lowest rotatory power (95·2° and 80·7).

Influence of the Naphthalene Group.

May I be allowed to refer briefly to the influence of the naphthalene group? On comparing the optical rotations of the menthyl esters of the two naphthylcarboxylic acids,‡ we observe in the *α* acid the influence of the neighbourhood of the second nucleus, but the difference between these acids and benzoic acid is, on the whole, of no great importance. We know from Bamberger's classical work that naphthalene is quite a different thing from benzene, but when we reduce one of its nuclei, the other, which does not carry the carboxyl-group, becomes a true benzenoid nucleus. We may therefore consider the hydro-aromatic acids as phenyl derivatives of cyclohexane-

* Tschugaeff, *Ber.*, **35**, 2759 (1912).
† Not yet published.
‡ Rupe and Silberberg, *Ann.*, **327**, 168 (1903); Rupe and Münter, *Ann.*, **373**, 121 (1910).

TABLE XIII.

	$[\alpha]_D$.	M_D.		$[\alpha]_D$.	M_D.
	79·08	—		91·30	—
	47·57	—		53·04	—
 *	—	92·1	 *	—	87·1
			$C_{10}H_{14}O : CH \cdot C_6H_5$	429·2	1020 Phenyl } Methylene camphor
			$C_{10}H_{14}O : CH \cdot C_{10}H_7$	340·0	986 α-Naphthyl } Methylene camphor

* The two optically active tetrahydronaphthoic acids have been prepared by Pickard and Yates, *Trans. Chem. Soc.*, **89**, 1104. Here the α-acid possesses in benzene solution the greater rotation.

carboxylic acids or as analogues of phenylacetic acid. In conjunction with Iselin* I was successful in preparing a series of derivatives of methylene camphor—for instance naphthylmethylene camphor. Its specific rotation is considerably less than that of phenyl methylene camphor (the benzylidene camphor of Haller); the molecular rotation is almost the same.

Theories as to the Influence of Unsaturation.

Until to-day we have had no satisfying explanation of the increasing effect of an unsaturated group, and still less of its opposite influences. The phenyl group and the double bond contain more energy than the saturated groups. Perhaps we shall be able to find here the germ of a theory; but in a recent paper Auwers, Eisenlohr and Roth† have shown that a conjugated double linking contains less energy than a non-conjugated, *i.e.*, that the former, in contradiction to its optical behaviour, is really the more saturated. So also the triple bond, in spite of its great energy-content, has generally a smaller influence on the rotatory power than the ethenoid bond. We must therefore look elsewhere for an explanation.

The molecular volume of unsaturated compounds is generally greater than that of saturated ones. This suggests the hypothesis that the influence of optically active groups is such that the four groups or radicals, which surround the asymmetric carbon atom, suffer a certain pressure or deformation from the larger volume.

That perhaps may give an explanation of the influence of an unsaturated complex near to the asymmetric carbon, but not of the strong effect of a remote unsaturated group, especially when there is an accumulation, unless we adopt the hypothesis of the lever mentioned by me just now.

When we try to deal with the theories of the supplementary valencies, perhaps in the light of Stark's hypothesis of the valency-electrons, we encounter the same difficulty; it gives an explanation for the reaction near the asymmetric carbon, but only of that.

In conclusion, I wish to discuss briefly the following question: Are we already able to make use of optical rotation as a help in determining the constitution of optically-active organic compounds? The refraction in many cases is of great value for this purpose. The optical rotation cannot yet be employed to the same extent, but I am of opinion that, in the hands of a chemist with some knowledge of this subject, this method may frequently be of real service.

May I be allowed to give here some examples borrowed from the work of others, as well as from my own? When I found, with Jäger,‡ that the product of the reaction of methyl magnesium bromide with citronellal gave a much larger rotation than the other alkyl-derivatives, for instance, the ethyl-compound, we could only suppose that in this methyl-compound (1) the double bond was nearer to the asymmetric carbon atom than in the other homologues, *i.e.*, the ethyl compound (2); this supposition was confirmed by oxidation with ozone. When, in the course of the same work, the allyl-derivative (3) showed a greater rotatory power than the corresponding propyl-compound (4), we were able to consider with much probability

* Rupe and Iselin, not yet published.
† *Ber.*, **43**, 1063 (1910); *Ann.*, **373**, 239 (1910).
‡ Rupe and Jäger, *Ann.*, **402**, 149 (1913).

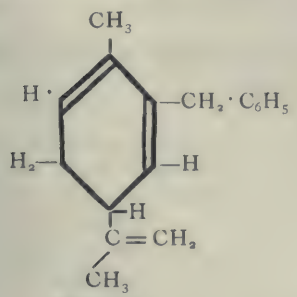
that the increased rotation was due to a conjugation, and this was confirmed by measurements of refraction.

(1) $C_6H_{11}\cdot CH(CH_3)\cdot CH:CH\cdot CH_3$ $[\alpha]_D = -10{\cdot}37$
methyl-compound

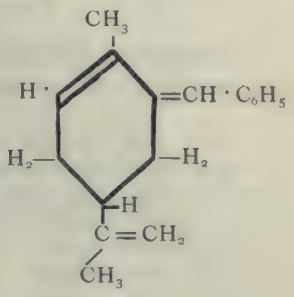
(2) $C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH_3$ $[\alpha]_D = -6{\cdot}640$
ethyl-compound

(3) $C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH:CH_2$ $[\alpha]_D = -10{\cdot}12$

(4) $C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH:CH\cdot CH_2\cdot CH_3$ $[\alpha]_D = -6{\cdot}68$.



Formula I.



Formula II.

On treating carvone with benzyl magnesium chloride* two isomeric hydrocarbons were obtained, the first with a great, the second with a rather low optical rotation. There is no doubt that the former has the Formula I, the latter the Formula II. The yield of these compounds being poor, we have not yet been able to determine the constitution in a chemical way. The refraction for both is nearly the same, and I do not think that oxidation would serve to differentiate the two compounds.

Every one who has worked in this field knows that the rotatory power is much more sensitive to changes of constitution than the refraction. One may recall how the transition of the enolic to the ketonic form of Forster's† benzoylcamphor is marked by the changing of the rotation, and we observe the same phenomena when the menthyl ester of phenylacetoacetic acid changes its rotation rapidly under the influence of piperidine.‡

One could easily multiply examples. There is, for instance, no doubt that when we have two isomeric unsaturated acids, both optically active, the one with the greater rotation possesses the double linking nearer to the asymmetric carbon. Trouble generally comes when phenyl groups enter the chain, and it is one of the problems of our science to find out the very complicated and irregular behaviour produced by the accumulation of unsaturated groups. The solution of this problem : 'tis a consummation devoutly to be wished !

* Rupe and Tomi, not yet published.
† Forster, *Trans. Chem. Soc.*, **79**, 994.
‡ Rupe and Lenzinger, *Ann.*, **395**, 91 (1912) ; **398**, 372 (1913).

THE ROTATORY DISPERSION OF TARTARIC AND MALIC ACIDS.

(Translated from the German.)

Professor H. Grossmann (Berlin) read a Paper on "The Rotatory Dispersion of Tartaric and Malic Acids."

Apart from the sugars, no class of optically active compounds has been so much investigated as that comprising the two oxyacids which are derived from succinic acid. This holds not only for tartaric and malic acids themselves, but also for their salts and organic derivatives. In this work specialists of all nations have participated, and in England numerous minute investigations have been carried out in recent years, especially by Percy Frankland, Patterson, and others, which have elucidated the relationship of optical rotatory power to various physical and chemical factors, notably to temperature and to solvents.

A comprehensive survey of the subject, which P. Walden elaborated in a lecture before the German Chemical Society in Berlin in 1905, has had an exceptionally stimulating effect on the work from a theoretical standpoint. Walden laid stress in this lecture on the great importance of the hitherto rather neglected property of rotatory dispersion, which he claims to be a property which illustrates in a striking manner the effect of the nature of the radicals attached to an asymmetric carbon atom. This lecture has, I freely admit, influenced very strongly the studies which I have made in recent years in the field of optical rotatory power.

I directed my attention first to the study of the neutral esters of tartaric and malic acids, and in conjunction with Rothgiesser and B. Landau I investigated in detail the effect of organic and inorganic solvents on the rotatory power of these esters at the ordinary temperature. For this purpose the rotatory dispersion of these solutions was always determined by the convenient method of Landolt, viz. by light-filters. It became very apparent from the exhaustive researches which were carried out with Landau, and which were published in 1910 in the *Zeitschrift für physikalische Chemie*, that a regular relation exists between the effect on the rotatory power of the active substance and the chemical nature of the optically inactive solvent. Further, it could be claimed with some certainty that the optically active esters of both acids are able to combine with the solvents to form more or less stable compounds, of whose existence there was no other indication than that deduced from optical properties. It is true that none of these compounds has as yet been isolated, but the magnitude of the changes in rotation, which afford an extremely delicate indicator for chemical reaction, makes the existence of these addition-compounds, at any rate in solution, highly probable.

The diagram (Fig. 1) shows the enormous effect of the solvent on the rotatory dispersion in dimethyl malate. It will be seen that the curve of

rotatory dispersion for the pure ester, which runs normally, can be deflected either to the right or to the left, and that between the maximum dextro-rotatory effect in solutions of the ester in arsenic trichloride and the maximum lævo-rotatory effect in phosphorus trichloride, chloral, bromal, pyridin, etc., there is a considerable difference. The existence of labile compounds is supported especially by the behaviour of dimethyl malate in nitrotoluene (Fig. 2), which shows that anomalous rotatory dispersion and change of sign of rotation

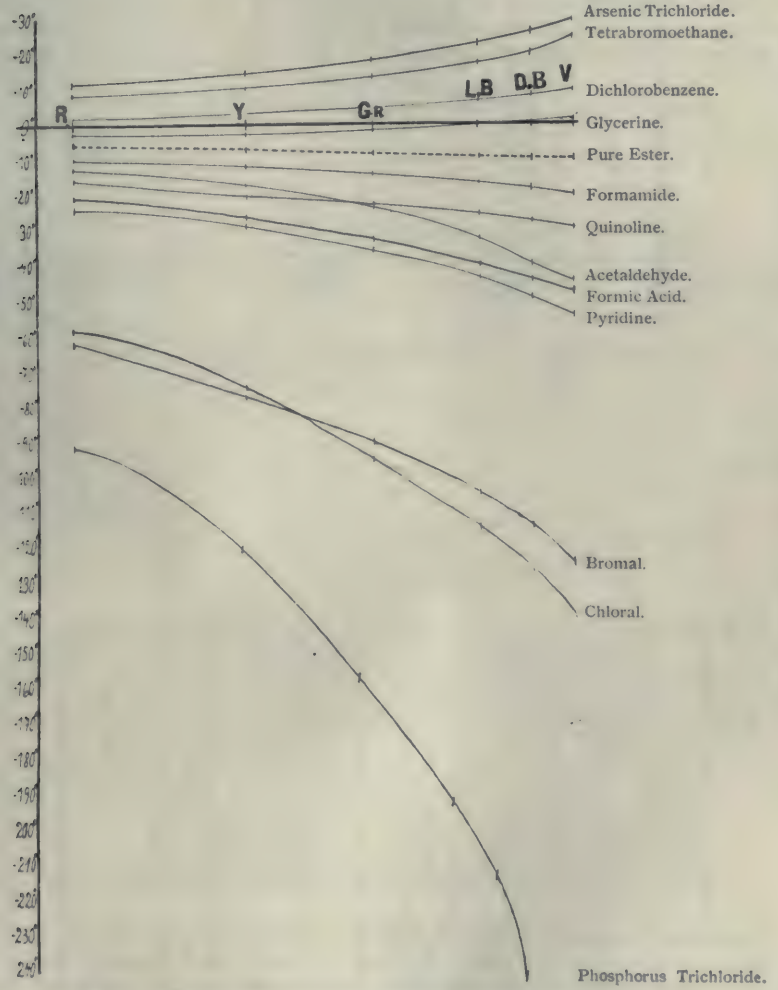
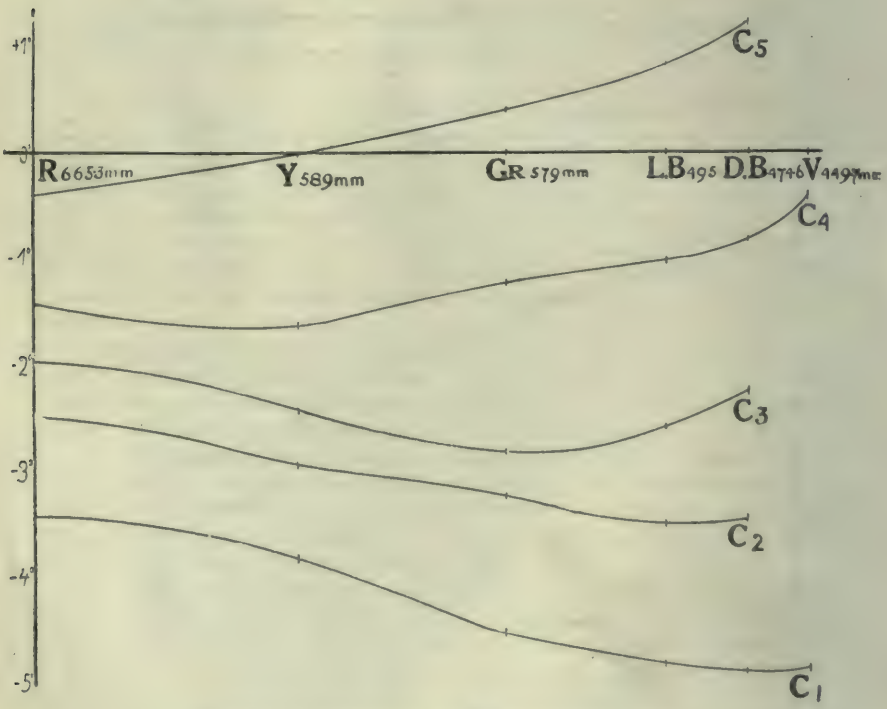


FIG. 1.—Solutions of Dimethyl Malate, Concentration 5 per cent.

are by no means so unusual as had hitherto been supposed. An explanation of these phenomena is given by the hypothesis of labile compounds in solution, whose rotation is opposite in sign to that which the pure substance possesses. Moreover, the great differences in rotation in the various solvents point to the same conclusion.

These phenomena were first recognized in tartaric and malic acids, and

numerous theories have been proposed to account for the facts. After having determined, however, that the influence of organic solvents on the rotatory power of both acids appears to be analogous to that of water, the phenomenon of anomalous dispersion loses its special character and falls into line with the theory. Nevertheless, one must remember that these two weak organic acids give more complex results than the neutral esters, because the former belong to the class of semi-electrolytes, and their aqueous solutions therefore contain different molecular groups with different optical activities. For example, in an aqueous solution of tartaric acid one must certainly expect to find the following groups: (*a*) Undissociated tartaric acid (lævo); (*b*) tartaric acid ions $C_4H_5O_6'$ and $C_4H_4O_6''$ (dextro) (the latter



CONCENTRATIONS.—$C_1 = 50$, $C_2 = 25$, $C_3 = 12{\cdot}5$, $C_4 = 5$, $C = 2{\cdot}5$.

FIG. 2.—Dimethyl Malate in *m*-Nitrotoluene.

being more strongly dextro-rotatory than the former); (*c*) hydrogen-ions; and (*d*) under certain conditions addition products of water and the acid. Under these circumstances it is not surprising that the rotation can be altered by the addition of organic compounds, which diminish dissociation; further, it must be noticed that, by the formation of more or less stable complexes between solvent and solute, an optical effect may arise which is opposed to that already mentioned.

I will now sketch the most important results of the work on tartaric and malic *acids* which I have carried out with Dr. Ascher and Dr. Grün, which support and amplify the results obtained with esters and the conclusions deduced therefrom.

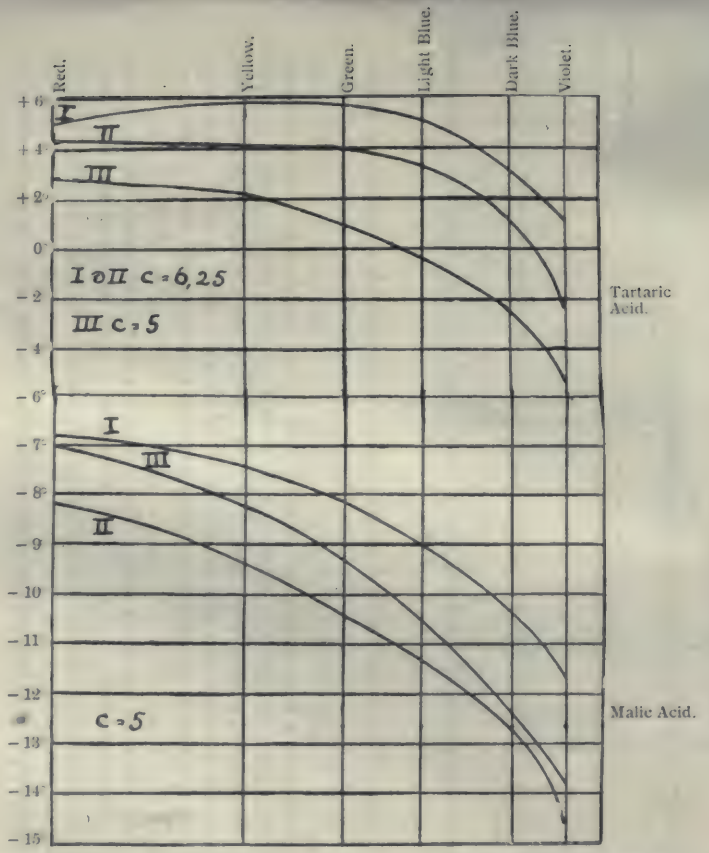
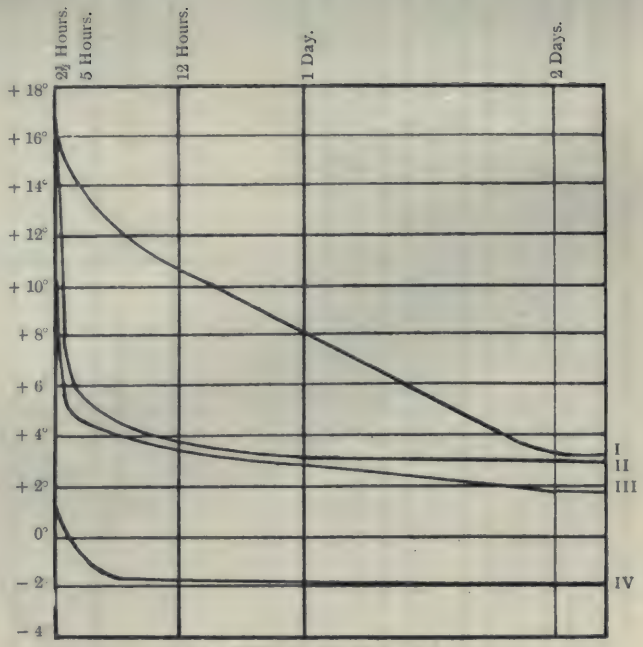


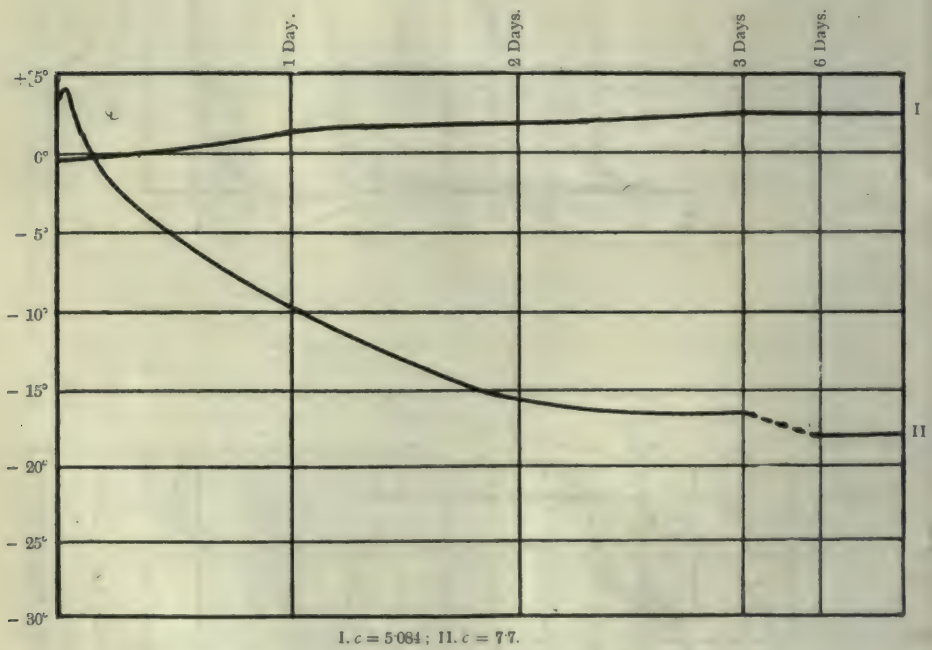
FIG. 3.—Rotatory-dispersion of Tartaric and Malic Acids in (I) Methyl Alcohol, (II) Ethyl Alcobol, (III) Propyl Alcohol.



I. $c = 4{\cdot}375$; II, III, IV. $c = 5$.

FIG. 4. — Mutarotation of Malic Acid in (I) Benzyl Alcohol, (II) Benzyl Alcohol and Benzene, (III) Benzyl Alcohol and Carbon Disulphide, (IV) Benzyl Alcohol and Methyl Alcohol.

I will begin with the alcohols of the aliphatic series, of which the lower members, especially methyl alcohol, are excellent solvents for tartaric and malic acids. The solvent power of propylalcohol for tartaric acid, on the other hand, is considerably less, so that it is not possible to obtain solutions stronger than 5 per cent. This fact by itself indicates that there is a much smaller affinity here between the acid and the alcohol, and it also bears out in every respect the other properties which have been observed in homologous series. In a 25 per cent. methyl-alcoholic solution of tartaric acid the phenomenon of anomalous dispersion is already apparent with a maximum effect in the green. With increasing dilution this maximum passes, in contradistinction to the behaviour in aqueous solution, towards the red end of the spectrum, so that the curve, instead of ascending from red to violet, descends. The dextro-rotatory power of tartaric acid is considerably diminished by



I. $c = 5{\cdot}084$; II. $c = 7{\cdot}7$.

FIG. 5.—Mutarotation of (I) Tartaric Acid and (II) Malic Acid in Formic Acid.

the alcohol, a fact which is evidently due to the diminution of dissociation of the acid. The effect in ethyl- and in propyl-alcohols, as might be expected is still greater, so that a reversal of rotatory power is observed in quite dilute solutions, whereas in aqueous solutions of tartaric acid it only occurs in quite concentrated solutions (66·5 per cent.) in the most refrangible rays (Fig. 3).

In the case of malic acid (Fig. 3, lower part of diagram), the addition of the alcohols merely causes an increase of lævo-rotation, and since there is no tendency towards change of sign the curve for rotatory dispersion also runs normally.

Since the dissociating power of aromatic alcohols is considerably smaller

than that of aliphatic alcohols, it is not surprising that the addition of benzyl-alcohol causes a further decrease in the dextro-rotation of tartaric acid. Whereas, however, tartaric acid is not soluble in benzylalcohol, malic acid behaves in a peculiar way, as Walden has already pointed out. Walden found that a solution of malic acid in benzylalcohol was strongly dextro-rotatory, but he overlooked the fact that this rotation changes with time and does not reach its constant value until after two days. How great the extent of this change is, may be seen in Fig. 4, which depicts the mutarotation curve of malic acid in benzylalcohol and benzene, benzylalcohol and carbon-disulphide, and benzylalcohol and methylalcohol. Benzylalcohol may be said, therefore, to react chemically with malic acid, and we may assume the action to be a gradual esterification.

A further interesting example of mutarotation was found in solutions of malic acid in pyridine. Here one observes a great increase in lævo-rotation,

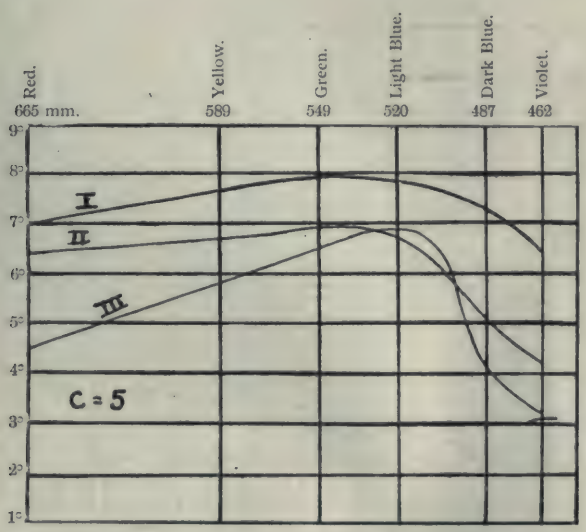


FIG. 6.—Rotatory-dispersion of Tartaric Acid in Mixtures of Equal Weights of Water and (I) Formic Acid, (II) Acetic Acid, (III) Propionic Acid.

which is probably due to salt-formation between malic acid and pyridine; but the formation of the pyridinium salt, which dissolves in excess of pyridine, occurs not immediately but gradually. The specific rotation after ten minutes in red light was $-9{\cdot}60°$ for a 5 per cent. solution of the acid, the value reaching $-20{\cdot}1°$ in the course of two days. Addition of benzene occasioned in this case also a more rapid change of rotation to a constant value.

Formic acid also produces a remarkable mutarotation both in tartaric acid and in malic acid (Fig. 5). It had already been observed that the esters of these acids, dissolved in formic acid, changed in rotatory power with time to a constant value, and further, in a former research with Bloch, proof was obtained that sugars exhibited mutarotation in formic acid solution.

As in the case of alcohols, the addition of organic fatty acids, of which

only the first three were investigated, caused the appearance of anomalous rotatory dispersion in both tartaric and malic acids (Fig. 6).

The effect of non-electrolytes, such as benzene and its homologues, and also such simple substitution products as halogen-benzenes, nitrobenzene, also various chlorine derivatives of acetylene, ethylene, and ethane, was quite analogous to their effect on esters of the two acids, namely, to produce a change in sign of the rotation. Since, however, none of these substances will

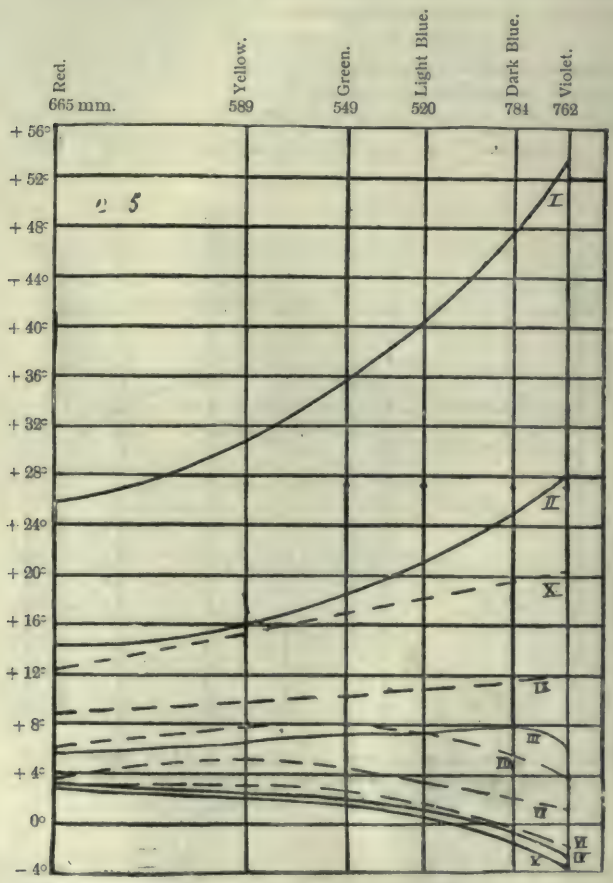


FIG. 7.—Rotatory-dispersion of Tartaric Acid in Mixtures of Sulphuric Acid and Water.

Full Curves I to IV, 95·60 to 63·50 per cent. H_2SO_4.
Dotted Curves VI to X, 50·73 to 0 per cent. H_2SO_4.

dissolve the free acids, mixtures with 25 or 50 per cent. of methylalcohol had to be used. All the cases of reversal of rotatory power and of anomalous dispersion that could be predicted from the theory were found in these experiments. All these substances are decided non-electrolytes, and must therefore favour the formation of undissociated molecules of the acid. Moreover, solutions with high percentages of these substances show lævo-rotation in tartaric acid and dextro-rotation in malic acid.

Whilst one must admit that certain theoretical difficulties exist in reference to these solvent-mixtures, it was possible to demonstrate quite clearly in another case that the magnitude of the rotation was influenced in a regular manner by the factors mentioned at the beginning. This is fully manifest from the behaviour of both acids towards sulphuric and phosphoric acids.

Contrary to the general view, that concentrated sulphuric acid always causes decomposition of these organic acids, it appears that even 100 per cent. sulphuric acid at the ordinary temperature dissolves both acids without

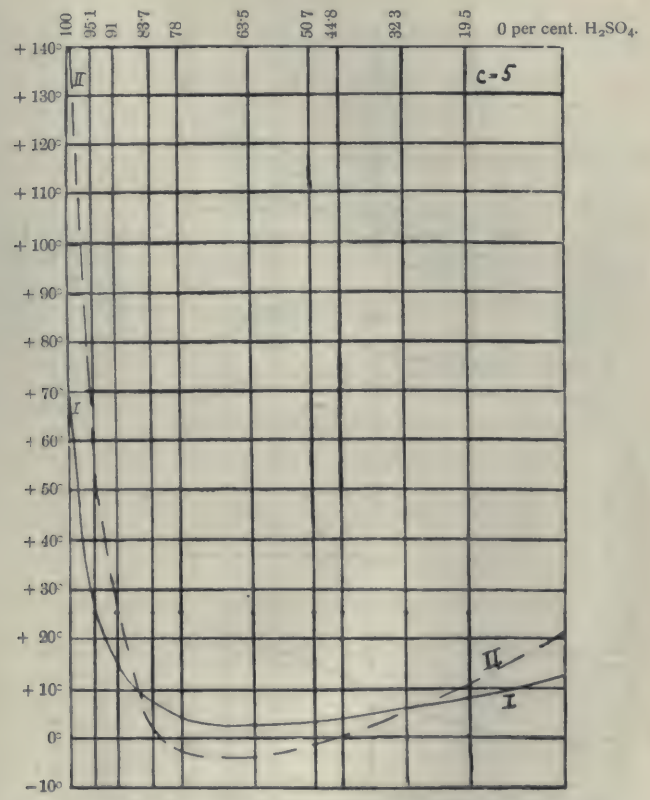


FIG. 8.—Rotatory Power of Tartaric Acid in Aqueous Sulphuric Acid for (I) Red, (II) Violet Light.

decomposition. In addition to this solvent, various mixtures of sulphuric acid with water were used, with the result that the phenomena of reversal of rotatory power and of anomalous rotatory dispersion were again observed (Figs. 7 and 8).

Malic acid gives similar results in sulphuric acid solution. The remarkable influence of pure sulphuric acid on the rotation is again shown, but here the maximum rotation is on the left. One may assume that at first the addition of sulphuric acid occasions a diminution in dissociation of tartaric and of malic acid, but that in those solutions which are rich in sulphuric acid

a conflicting influence is felt, which is evidently attributable to the formation of an additive compound or a sulphuric acid ester.

The phenomena are quite similar in the case of phosphoric acid, which, however, could only be used in 84 per cent. solution. With tartaric acid, the most concentrated phosphoric acid solution gave the greatest depression, but all the values are still on the dextro side, and all the solutions give anomalous dispersion (Fig. 9); on the other hand, the solutions of malic acid in dilute phosphoric acid solutions show a reversal of rotatory power from left to

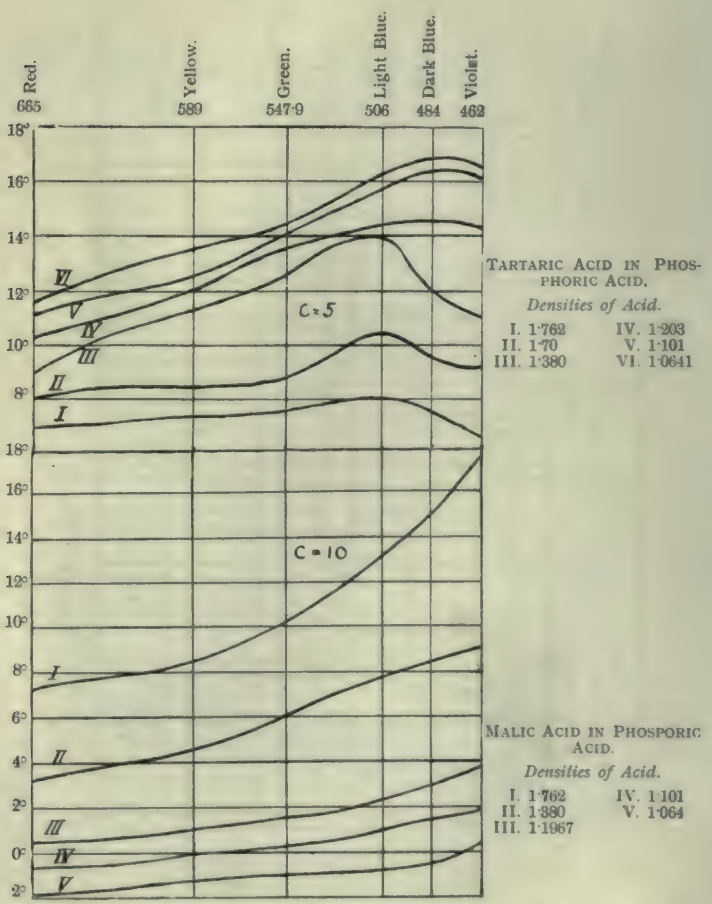


FIG. 9.—Rotatory-dispersion of Tartaric and Malic Acids in Aqueous Phosphoric Acid.

right, those in concentrated phosphoric acid being strongly dextro-rotatory. The phenomena in both the inorganic acids correspond completely, so far as comparison is possible.

Reviewing the results of this work, one must admit that they strongly support the views expressed at the outset, since measurements of rotatory dispersion always give much clearer results than observations with mono-

chromatic light. In an investigation on menthone, which I have carried out with Dr. Brauer, it could be shown that, by neglecting the measurement of dispersion and by limiting observations to monochromatic light, false conclusions could be made. It is of great general importance, therefore, especially when working with substances whose specific rotation is not great, never to omit the measurement of rotatory dispersion, which may throw much light upon the subject, still in need of full explanation, of the relation between solvent and solute.

ANOMALOUS ROTATORY DISPERSION.

A Paper by **Professor Leo Tschugaeff**, of the Royal University, St. Petersburg, on "Anomalous Rotatory Dispersion" was communicated by Dr. T. Martin Lowry.

It has been well known since Biot's classical work on rotatory polarization that most of the colourless active bodies exhibit "normal" rotatory dispersion, the numerical values of the optical rotation continuously increasing with decreasing wave-length.*

The dispersion ratios $\frac{[\alpha]_F}{[\alpha]_C}$ of compounds of this class vary for the most part within the limits 1·8-2·0. Quartz, cane sugar, different active hydrocarbons, and alcohols may be cited as examples of such bodies.

Biot was also the first to point out that there are several exceptions to this rule, which belong to the domain of "anomalous" rotatory dispersion. This term is generally applied to those cases in which the optical rotation passes through a maximum or through a zero value or decreases with decreasing wave-length. The rotation and dispersion of these substances are, however, largely influenced by the *temperature* and by the nature of the *solvent*, so that a substance which shows anomalous rotatory dispersion under some conditions may become normal under other conditions.

In the present state of our knowledge we can assume that all the cases of anomalous rotatory dispersion hitherto described may be divided into three classes.

1. To the first class belong all those cases in which anomalous dispersion is due to the *superposition* of the optical rotations of two (or more) *different kinds of normally dispersing molecules* differing in rotatory dispersion as well as in the sign of their rotation.

It was shown by Biot that dispersion of this kind may be observed in mixtures of dextro-rotatory camphor with lævo-rotatory oil of turpentine, and Arndsen † put forward the supposition that the anomalous dispersion of tartaric acid is due to the same cause. Mixtures of *l* menthon with isomenthone ‡ may be cited as a further example.

2. Another type of anomalous rotatory dispersion is intimately related with the existence of *absorption bands* in the spectra of the active compounds in question. The discovery of this type is due to the French physicist, A. Cotton.§

Cotton pointed out in 1896 that the dispersion curves of certain coloured

* Cf. H. Landolt, *Das Optische Drehungsvermögen*, II. Aufl., Braunschw., 1898; P. Walden, *Berl. Ber.*, **38**, 345 (1905).

† *Ann. de chem. phys.*, [3], **54**, 858 (1858).

‡ L. Tschugaeff, *Zeitschr. f. physik. Chemie*, **76**, 469 (1911).

§ A. Cotton, *Recherches sur l'absorption et la dispersion de la lumière par les milieux doués du pouvoir rotatoire*. Thèse, Paris 1896.

solutions, containing, for example, double tartrates of copper or of chromium, go through a maximum in the next neighbourhood of the absorption band, the sign of the rotation being subsequently changed and the curve going through a second maximum of the opposite sign.

Cotton has shown further that the anomalous dispersion in absorbing bodies is intimately allied with the so-called circular dichroism, that is to say the two circular rays resulting from the original plane vibration are not equally absorbed by the active body.

It is well to mention here that Drude,* to whom we are indebted for a general electronic theory of dispersion, has shown that this theory is quite in accordance with Cotton's experimental results.

Cotton carried out his remarkable investigation with solutions of complicated composition ; he was not able to isolate his active complex salts nor to obtain them in the state of purity. The same is true of the subsequent measurements of McDowell† and of Grossmann,‡ who repeated and extended Cotton's experiments.

Five years ago I discovered § a series of coloured and active compounds showing anomalous rotatory dispersion of the same type as Cotton's double salts. These compounds were derivatives of the menthyl-, bornyl- and fenchyl-xanthates and of the corresponding thiourethanes.

It was pointed out that there is a general parallelism between the absorption spectra of these bodies and the shape of their dispersion curves.‖ A still closer parallelism holds between the dispersion and absorption produced by one and the same active body in different solvents, the absorption and the dispersion curves being always displaced in the same direction by passing from one solvent (toluene) to another (acetone).

On the other hand evidence was brought forward that the anomalous dispersion was not due to the influence of the solvent, since the compounds in question showed this property also in a state of superfusion.¶ But still more noteworthy is the recent work of Bruhat** and Cotton,†† who succeeded in observing circular dichroism in one of my substances—1 : 2-diphenyl-3-*l*-bornylimido xanthide—of the following constitution—

$$C_6H_5\text{-}CS\text{-}N(C_6H_5)\text{-}CS\text{-}OC_{10}H_{17},$$

and pointed out that the connection between this phenomenon and the sign of the optical rotation in both the antipodes is exactly the same as is required by theoretical considerations.

During the investigations performed in my laboratory it was shown that abnormalities may occur in the shape of the dispersion curve of an active and colourless compound if it exhibits an ultra-violet absorption band in the neighbourhood of the visible spectrum.‡‡

* *Optik*, 1906.
† *Physical Review*, 1905, 163.
‡ *Chem. Centralblatt*, 1908, II, 1996 ; *Zeitschr. f. physik. Chemie*, **72**, 93 (1910).
§ L. Tschugaeff, *Berl. Ber.*, **42**, 2244 (1909).
‖ L. Tschugaeff und A. Ogorodnikoff, *Zeitschr. f. physik. Chemie*, **74**, 503 (1910) ; **79**, 481 (1912).
¶ L. Tschugaeff und A. Ogorodnikoff, *Ann. Chim. Phys.*, [8], **22**, 137 (1911).
** G. Bruhat, *Comptes Rendus*, **153**, 248 (1911).
†† A. Cotton, *Comptes Rendus*, **153**, 245 (1911).
‡‡ L. Tschugaeff, *Zeitschr. f. physik. Chemie*, **76**, 469 (1911) ; *Bull. Soc. Chim.*, [4], **11**, 718 (1912). L. Tschugaeff et A. Kirpitcheff, *Bull. Soc. Chim.*, [4], **13**, 796 (1913).

Thus the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ of many ketones goes far beyond the normal limits mentioned above, *e.g.* :

Substance.	$\frac{[\alpha]_F}{[\alpha]_C}$.	Solvent.
Camphor	2·69	Methylic alcohol
Epicamphor	2·76	Methylic alcohol
aa-Dibromcamphor	3·13	Benzene
aa-Diiodocamphor	3·41	Benzene
Dihydrocarvone	3·30	None
Pulegone	2·76	None
1-Methyl-cyclohexan-3-one	3·50	None
Nopinone	3·75	None
Pinonic acid	2·63	Methylic alcohol

The dispersion curves of such ketones for the most part cannot be expressed by the simple formula given by Drude—

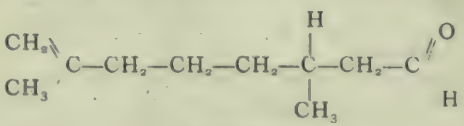
$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

Moreover, the rotations are influenced very largely by the nature of the solvent, just as is the case in substances showing anomalous rotatory dispersion.

On the other hand it is well known that the ketones exhibit a general absorption band at about 3,500–3,800 A.U., whereas the saturated hydrocarbons and alcohols are practically diactinic for these radiations. We are therefore justified in concluding that the exaltation of the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ in the ketones is intimately associated with the nature of the absorption spectra of these compounds.

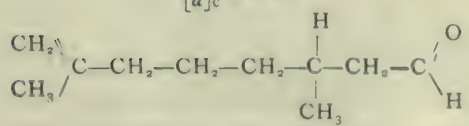
As a matter of fact it was shown by Darmois* that camphor exhibits the typical form of anomalous dispersion in the neighbourhood of the ultra-violet absorption band.

Quite the same seems to be true in the case of *aldehydes*, which, like the ketones, show selective absorption in the ultra-violet, as was pointed out recently by Henry and others. Miss S. Matthiesen undertook at my suggestion the optical study of the following members of the citronellal group :



Citronellal.

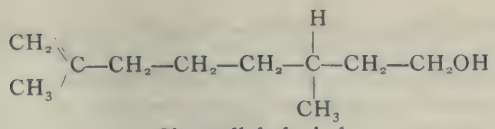
$\frac{[\alpha]_F}{[\alpha]_C} = 2{\cdot}42.$



Dihydrocitronellal.

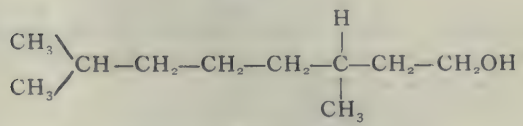
$\frac{[\alpha]_F}{[\alpha]_C} = 2{\cdot}40.$

* E. Darmois, *Recherches sur la polarisation naturelle et la polarisation rotatoire magnétique.* Thèse, Paris, 1910.



Citronellyl alcohol.

$$\frac{[\alpha]_F}{[\alpha]_C} = 2{\cdot}04.$$



Dihydrocitronellyl alcohol.

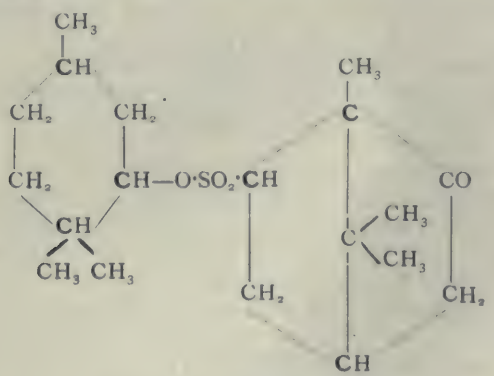
$$\frac{[\alpha]_F}{[\alpha]_C} = 1{\cdot}93.$$

It will be seen that the aldehydes examined possess almost as high a dispersion as many ketones, whereas the corresponding alcohols give quite normal dispersion ratios.

3. We may now turn to the third and last type of anomalous rotatory dispersion.

It was recently shown by the author * that anomalous dispersion may be produced by the *superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body*, the necessary condition being that these partial rotations should be of *opposite sign* and should possess *different dispersion ratios.*

As an example of bodies which belong to this type, menthyl β-camphorsulphonate may be cited, the two centres of activity being the menthyl and the camphor radicles :



R. W. Wood † has recently pointed out that there must exist a special case of anomalous dispersion which he denotes as "spurious," which is intimately related to the type just alluded to. Wood concluded from theoretical considerations that anomalous dispersion must ensue if we have two electrons in an active molecule, one in the infra-red and the other in the ultra-violet. If these electrons rotate in the same direction, the rotation may be expected to go through a zero value near the middle of the visible

* L. Tschugaeff, *Berl. Ber.*, **44**, 2023 (1911). L. Tschugaeff und G. Glinin, *Berl. Ber.*, **45**, 2759 (1912).

† *Physical Optics*, New York, 1911.

spectrum, whilst if they are of opposite sign, one being dextro-rotatory and the other lævo-rotatory, the rotation will have a minimum value. In Professor Wood's opinion the case of tartaric acid is of this type.

It is well to bear in mind also that each anomalous dispersion curve must necessarily be influenced by the superposition of the consequent partial rotations if more than one asymmetric carbon atom (or generally more than one centre of activity) is present in the molecule of the active substance.

For this reason it is not surprising that there is no complete parallelism * between the presence of an absorption band and the appearance of anomalous dispersion in the visible spectrum.

Thus menthyldixanthogenide, $C_{10}H_{19}$—OCS—S—S—CSO—$C_{10}H_{19}$, and bornyldixanthogenide, $C_{10}H_{17}$—OCS—S—S—CSO—$C_{10}H_{17}$, exhibit anomalous rotatory dispersion within the limits of the visible spectrum, whilst the fenchyldixanthogenide (isomeric with the bornyl derivative just mentioned and possessing a similar spectrum) does not possess this property.

In order to clear up the nature of the dispersion curves resulting from optical superposition it is necessary to examine first if the superposition rule is generally valid, and secondly in what degree these partial rotations themselves are influenced by mere constitutional factors.

The principle of optical superposition, first suggested by Van't Hoff,† was subsequently subjected to an experimental test by Guye and Gautier ‡ and by Walden ‖ and recognized as valid. Recently, however, Rosanoff ‡ and Patterson § and his pupils put forward theoretical objections and experimental evidence against the validity of this principle, their arguments being based on a comparison of the optical rotation produced by the methyl esters of the isomeric diacetyltartaric acids.

According to the theory of optical superposition the rotation of the ester corresponding with mesotartaric acid should be equal to half of the sum of the rotations produced by the ester of *d* and *l* tartaric acids. The maximum departure from the theoretical value in the experiments of Patterson amounted to 18 per cent. But the rotation values of these esters are largely influenced by the nature of the solvent used, and Van't Hoff suggested therefore that analogous experiments should be made in more comparable conditions.

As a matter of fact, experiments performed by Mr. Glebko at my suggestion with *l* menthyl and fenchyl urethanes of the isomeric diethyltartrates gave much better agreement with theoretical values, the difference varying from 1 to 5 per cent. Consequently the superposition rule seems to be valid at least to a first approximation.

Experiments quite recently performed in my laboratory have shown that the dispersion curve of an active substance is influenced not only by the absorption bands, but by the distance of the centres of activity from the chromophores of the active molecule. Thus a chromophore group situated in the neighbourhood of a centre of activity may produce anomalous dispersion within the limits of the visible spectrum, whilst if sufficiently remote from such a centre its influence on the shape of the dispersion curve may be small or negligible.

* L. Tschugaeff und A. Ogorodnikoff, *Zeitschr. f. physik. Chemie*, **85**, 481 (1913).
† Cf. Van't Hoff, *Lagerung der Atome in Raume*, III Aufl., Braunschweig, 1908.
‡ Rosanoff, *Zeitschr. f. physik. Chemie*, **56**, 565 (1906).
§ T. S. Patterson, *Journ. Chem. Soc.*, **89**, 1939 (1906); **91**, 705 (1907).
‖ *Berl. Ber.*, **46**, 2752 (1913).

To take an instance, of the two metameric esters corresponding to *l* menthol—

$$C_{10}H_{19}\text{-}OCS\text{-}S\text{-}CH_2\text{—}COO\text{-}CH_2\text{-}C_6H_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad I$$

$$C_6H_5\text{-}CH_2\text{-}OCS\text{-}S\text{—}CH_2\text{-}COOC_{10}H_{19} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad II$$

it is only the first (I) which shows anomalous dispersion in the visible region, the dispersion of the ester II being quite normal.*

Now in the ester I the chromophorous group CS-S is separated from the active radicle $C_{10}H_{19}$ only by a single oxygen atom, whilst in the second ester these two radicles are separated by a chain of three atoms

$$\text{—C—C—O—}$$

The above conclusion is quite analogous with a rule put forward by the author some sixteen years ago† for optical rotations corresponding with one definite ray of the spectrum, namely the D line of sodium. According to this rule the influence of an inactive substituent introduced into an active molecule at a point sufficiently remote from the centre of activity is very small, but its influence attains its highest value if the place occupied by the substituent is in the neighbourhood of the inactive complex.‡

It is particularly noteworthy that the radicles, the introduction of which into the molecule of an active substance causes the rotation values for the most part to be raised (*e.g.*, the radicles with a double linkage, the aromatic groups, etc.), and the chromophores which are responsible for anomalous dispersion possess the same chief feature, for they are both *unsaturated* groups.

In the author's opinion the modern electronic theory of rotatory polarization and dispersion created by Drude§ is capable of throwing some light on this question and of giving a rough idea of the influence which the constitutional factors just considered may exert on the sweep of the dispersion curve.

Drude has put forward the idea that optical rotation is due to a peculiar form of electronic motion. He assumes that the dispersion electrons which are capable of being set in vibration by the impacts of the light waves are forced in active bodies to move to and fro in a spiral path instead of along straight lines, the direction of the motion corresponding with the sign of the rotation. This motion is obviously due to the asymmetric distribution of matter within the molecules of the active compounds.

Drude makes no special hypothesis as to the position occupied by the active electrons, but it seems reasonable to suppose that the most active of them are attached to the asymmetric carbon atom itself, or are situated in the immediate neighbourhood of the centre of activity. As regards the other electrons which come into play in rotatory dispersion, we can assume that their activity is diminished with increasing distance from the asymmetric complex.

* This work (not yet published) was performed at my suggestion by Mr. W. Lebedinski.

† *Berl. Ber.*, **31**, 360, 1775, 2451 (1898); *Journal of the Russian physik. Chem. Society*, (II), **29**, 122, 227 (1897); **30**, 18, 51, 188, 217 (1898); (I), **34**, 600 (1902).

‡ These conclusions are by no means altered by the results of the very beautiful work of Messrs. Pickard and Kenyon, which show secondary irregularities in the rotation curves in homologous series at points at which the carbon chain can return upon itself (R. H. Pickard and J. Kenyon, *Journ. Chem. Soc.*, **99**, 45: **101**, 620, 1427; **103**, 1923). See also the very remarkable Presidential Address by P. F. Frankland (*Journ. Chem. Soc.*, **101**, 656).

§ *Optik*, 1906.

In the spectrum of colourless saturated organic compounds there seems to exist a very deep band (or several bands) in the inaccessible ultra-violet, and it is very probable that to this band is due the general shape of the "normal" dispersion curve, its "anomalous" portion being restricted to the neighbourhood of the band.

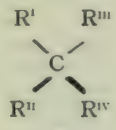
This view is in accordance with the results recently obtained by T. M. Lowry* in his very remarkable investigations on both magnetic and optical rotatory dispersion. Lowry pointed out that the dispersion of many colourless active compounds in the visible spectrum may be represented by means of an equation given by Drude with but two constants:

$$a = \frac{k}{\lambda^2 - \lambda_0^2},$$

λ_0 being the wave-length of the remote ultra-violet band.

If, however, the substance in question possesses another absorption band within the limits of the visible spectrum, the dispersion curve becomes anomalous in the accessible spectral region, and even if the selective absorption occurs in the near ultra-violet, as in the case of the ketones above mentioned, the shape of the curve corresponding to the visible part betrays the neighbourhood of an absorption band, the dispersion ratios assuming abnormally high values.

Let us first turn our attention to colourless compounds and consider in what manner the different inactive radicles of an asymmetric molecule—



containing but one asymmetric carbon atom, can influence the rotation value and the shape of the dispersion curve.

As we have seen, the chief part of the optical rotation will be produced by the electron (or electrons) attached to the asymmetric carbon atom itself and will remain in direct relation to the deviation of the spiral path along which the electron moves from a straight line. Now it may be admitted that this deviation should be proportional to the degree of asymmetry of the molecule as measured by the product of the differences of four constants, K_1, K_2, K_3, and K_4, corresponding with the four groups R', R'', R''', and R'''' of the molecule $CR'R''R'''R''''$, as was originally suggested by Ph. A. Guye† and by Crum-Brown.‡

$$P = (K_1 - K_2)(K_1 - K_3)(K_1 - K_4)(K_2 - K_3)(K_2 - K_4)(K_3 - K_4).$$

Perhaps we should not be far from the truth if we assume further with Guye that the variables $K_1 \ldots K_4$ are functions of the masses of the radicles attached to the asymmetric atom, although we do not know the exact nature of this function; but in any case, if these four groups differ materially in their degree of saturation, we shall still have to consider the influence of another constitutional factor on rotation; thus, it would be expected that strongly un-

* T. M. Lowry, *Phil. Trans.*, **212**, 261 (1912); *Journ. Chem. Soc.*, **103**, 1062 (1913); T. M. Lowry and T. W. Dickson, *Journ. Chem. Soc.*, **103**, 1067 (1913); *Proc. Chem. Soc.*, **29** (1913).

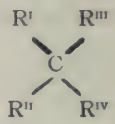
† Ph. A. Guye, *Étude sur la dissymetrie moléculaire*, Genève, 1891.

‡ Professor Crum-Brown, *Proc. Roy. Soc. of Edinburgh*, 1890, 181.

saturated radicles containing free-movable electrons would exert a considerable influence on the electric field produced by the molecule, the differences $K_1 - K_2 \ldots$ being much larger if K_2 corresponds with a saturated group and K_1 to an unsaturated one than if both the groups are nearly equally saturated.

From this point of view it may easily be understood why the influence of unsaturated groups on the rotation values is considerable only when in immediate proximity to the asymmetric carbon atom.*

On the other hand, the rotation and dispersion produced by an active molecule



may be influenced by the vibration of the electrons attached to the radicles R', R'', R''', R'''', as well as to the asymmetric carbon atom itself, for the asymmetry of the field within the molecule must cause all these electrons to move along spiral paths. Consequently, each radicle must contribute by means of its electrons to the value of the optical rotation produced by the molecule as a whole, and (the free periods of these electrons being in general different) also to the resulting dispersion. It may be noted also that it is by no means necessary that the electrons in the four radicles and in the central atom should rotate in the same direction. Consequently it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion. The anomaly will be due in this case to the superposition of the effect produced by the electrons attached to the different radicles of the same molecule. The question as to whether such cases can be realized in practice can be settled only by experiment, but it is possible that some cases of anomalous rotatory dispersion quite recently noticed by R. H. Pickard and J. Kenyon † should be classed in this category.

Time will not permit of further discussion of the influence of chemical constitution on the rotatory dispersion in active compounds, but I should like before concluding to touch briefly upon an allied question which claims a very considerable interest.

It was pointed out by Chr. Winther ‡ and by P. Walden § that the dispersion curves of several anomalously dispersing bodies are largely influenced by the temperature at which their rotations are taken and by the nature of the solvent used.

It seems to be the current opinion that this particular behaviour is due to a displacement of equilibrium between the two (or more) different kinds of molecules which are assumed to constitute the active substance.

A quite different hypothesis, however, was put forth recently by R. W. Wood, the distinguished American physicist. He assumes, as previously mentioned, that the anomalous dispersion of tartaric acid may be due to the existence of two active electrons in its molecule.

This hypothesis is in complete accord with the view just put forward, that

* It seems to be permissible in this case, at least to a first approximation, to compare the effects produced on the rotation by different substituents entering into the molecule for one determined wave-length, *e.g.*, for the D sodium line, as has so often been done.

† *Proc. Chem. Soc.*, **29**, 296 (1913).

‡ Chr. Winther, *Zeitschr. f. physik. Chemie*, **41**, 161 (1902); **45**, 331 (1903).

§ P. Walden, *Berl. Ber.*, **38**, 345 (1905); *Zeitschr. f. physik. Chemie*, **55**, 1 (1906).

several electrons may be active in a molecule containing but one asymmetric carbon atom, in which case the rotatory power as well as the dispersion of the substance in question will be equal to the sum of the effects produced by its several active electrons.

On the other hand, it is very probable (1) that the configuration of the molecule, and consequently the degree of asymmetry of the corresponding asymmetric field, is a function of the temperature, and (2) that the intensity of this field is not equally influenced in its different parts by the same rise of temperature.

It seems to be quite possible, therefore, that the influence of different active electrons may become dominant at different temperatures, and that a substance which possesses normal rotatory dispersion at a certain temperature t_1 may become anomalous at another temperature t_2. It is, however, very difficult in the present state of our knowledge to distinguish between such a case and the case of a mixture of two active bodies which present anomalous dispersion at certain temperatures only.

Similar considerations may apply in relation to the influence of solvents on anomalous rotatory dispersion. It is, therefore, easy to understand that, from the above point of view, active bodies which are especially sensitive to the influence of the temperature and of the solvents must have a marked tendency to present the phenomenon of anomalous rotatory dispersion.* Since nearly the whole of the experimental data concerning the influence of temperature and of the solvent on anomalous rotatory dispersion have been derived from derivatives of tartaric and malic acid,† it seemed advisable to undertake analogous experiments with active bodies representing the different types of anomalous dispersion above mentioned. This work has been carried out in my laboratory in conjunction with Messrs. Pigoulewsky, Pastanogoff, and Ogorodnikoff.‡

The results obtained have two important bearings : firstly, they show that sensibility to the influence of temperature and to the nature of the solvent is not confined to colourless bodies exhibiting anomalous dispersion of the type of tartaric acid, but occurs also in substances exhibiting Cotton's phenomenon and in those which possess anomalous dispersion due to intramolecular optical superposition.

It may be noted also that this sensibility can be very different in closely related substances. To take an instance, the dispersion of the thioanhydride of the menthylxanthogenic acid $C_{10}H_{19}O\text{-}CS\text{—}S\text{—}CS\text{-}O\text{—}C_{10}H_{19}$ is very considerably influenced by temperature, while the sensibility of the corresponding fenchyl derivative is quite insignificant, in spite of the fact that both dispersion curves are nearly identical in shape.

Secondly, it follows from our experiments that in many cases the anomalous dispersion curves are shifted by the influence of temperature or by the nature of the solvent in the same direction as in the case of tartaric acid and its esters. For instance, the behaviour of the thioanhydride of menthylxanthogenic acid $C_{10}H_{19}\text{-}OCS\text{-}S\text{-}CSO\text{-}C_{10}H_{19}$ towards temperature and the influence of different solvents on the dispersion of menthyldixanthogenide,

* Quite recently R. H. Pickard and J. Kenyon stated that certain esters containing but one asymmetric carbon atom exhibit anomalous rotatory dispersion at high temperatures as well as in several solvents (*Proc. Chem. Soc.*, **29**, 296 (1913)). In the author's opinion this effect may be due to the intramolecular superposition of the effects produced by several active electrons.

† *Zeitschr. f. physik. Chemie*, **85**, 481, 553 (1913).

‡ The details of the experiments of R. H. Pickard and T. Kenyon above mentioned are not yet available.

$C_{10}H_{19}OCS—S\text{-}S—CSO\text{-}C_{10}H_{19}$ may be cited. In both cases the curves are at the same time raised and shifted to the violet end of the spectrum, precisely as Winther and others have observed is the case in the tartaric series. This analogy is a very remarkable one, and whatever its final interpretation may be, there is no doubt that there must exist some intimate relation as to the origin of the anomaly in both cases.

ON THE EXISTENCE OF RACEMIC TARTARIC ACID IN SOLUTION.

(Translated from the French.)

Dr. E. Darmois (Paris) sent in a Paper "On the Existence of Racemic Tartaric Acid in Solution," which was read by Dr. H. Borns.

In a previous research * I have shown that the study of the rotatory dispersion could render considerable service in the study of mixtures. As regards a numerous category of bodies (essential oils and their derivatives) in particular, I have pointed out a certain number of verifications of the following principle: "If we mix the two optical inverts of one and the same body in different proportions, the rotatory dispersion of the mixture is equal to that of the two active varieties." The rotatory power is *unique* (independent of the solvent and of the concentration) for all the bodies in question; it is the same for all the mixtures of the two inverts; it is a characteristic property of the chemical species studied.

It appeared interesting to investigate from this point of view mixtures of dextro-tartaric acid and lævo-tartaric acid. We know that it is very easy to obtain, by mixing the two acids in equal proportions, the formation of the racemic acid whose properties are distinctly different from those of the two active varieties. One might therefore think that the formation of the racemic acid—consequently supposing mutual actions in the mixture—should be capable of modifying the rotatory power of the mixture.

The specific rotatory power of tartaric acid in aqueous solution is variable; the rotatory power varies in a continuous manner when we change the concentration. In a diluted solution the rotatory power is large, and the dispersion is normal; in concentrated solution the rotatory power is small, and the dispersion is abnormal. The lævo-acid offers the same phenomena in an inverse sense. The rotatory power of the dextro-acid has been studied by Arndtsen,† who has given formulæ permitting of calculating at the temperature of 25° C., the rotatory power of the acid for the radiations C, D, E, C_2, F, *e* of the solar spectrum. For the D line, *e.g.*, we have $[a] = 14{\cdot}98 - 0{\cdot}1303\,p$, where p designates the weight of acid in 100 g. The experiments of Arndtsen have been resumed by Wendell,‡ whose results, though slightly different, also lead to linear functions.

When we mix the two acids (the dextro and lævo) in different proportions, we shall obtain acids whose activity will pass, in a continuous manner, from that of the dextro-acid to that of the lævo-acid. Each of these acids must *a priori* have its variable rotatory power and variable dispersion.

Suppose we take 20 g. of tartaric acid, consisting of 14 g. of dextro-acid and 6 g. of lævo-acid, dissolve the 20 g. in water, and dilute the solution to

* *Ann. de Chim. et Phys.*, ser. viii., **22**, p. 247.
† Ibid., ser. iii., **54**, p. 858.
‡ *Wied. Ann.*, **66**, p. 1152 (1898).

100 cm.³. The total concentration of tartaric acid is 20 g.; for such a concentration the dispersion of a dextro-acid solution is anomalous. Two hypotheses then appear possible: (1) the two acids are merely mixed in the solution which possesses the dispersion of the acid at the concentration 20 (anomalous); (2) the two acids are combined in the solution; the 100 cm.³ therefore contain 12 g. of racemic acid (inactive) and 8 g. of dextro-acid; the concentration of the dextro-acid is 8; the solution possesses the dispersion of the dextro-acid at concentration 8 (normal). We shall see that the determinations enable us to decide in favour of the first hypothesis.

The measurements have been made for the mercury lines of wave-lengths 578, 546, 492, 436 $\mu\mu$; these lines are respectively near to the lines D (589), E (527), F (486), and *e* (438). It would be desirable to extend the formulæ of Arndtsen to the mercury lines which are at present commonly used in polarimetry. As I could not make these determinations for want of time, I shall in the following considerations apply the formulæ of Arndtsen. I shall give particulars of one series of measurements only which I have made with a solution of dextro-acid for the purpose of comparing the results with those deduced from Arndtsen's formulæ.

A. *Investigation of a Solution of Dextro-acid.*—The solution contained 9·66 g. of dextro-acid in 19·73 g. of water; $d = 1{\cdot}175$, $p = 32{\cdot}9$, $C = pd = 38{\cdot}64$, $t = 20°$ C.

Rotations measured in 20 cm.	578	546	492	436
	7·90°	8·31°	8·65°	6·90°

The dispersion is clearly anomalous. The formulæ of Arndtsen yield for

	D.	E.	F.	*e*.
at 25° C.	8·35°	9·20°	9·65°	8·86°.

Reducing the rotations observed to 20° C. by means of Wendell's coefficient we find

	D.	E.	F.	*e*.
at 20°	7·80°	8·45°	8·70°	(not studied by Wendell.)

The calculated results approximate the experimental values very closely; the concordance is of the order of those which we shall meet with in the following considerations.

B. *Mixtures of Dextro-acid and Lævo-acid.*—It is necessary to select a solution such that the total concentration corresponds to an anomalous dispersion, whilst the concentration in *remaining* acid corresponds to a normal dispersion. We are further limited as to concentration by the fact that the racemic acid is little soluble in water. I give particulars of one of the solutions investigated.

Dextro-acid 4·10 g., lævo-acid 2·00 g., water 21·64 g.; $d = 1{\cdot}101$.

Rotations measured in 20 cm.	578	546	492	436
	2·18°	2·33°	2·45°	2·35°

The dispersion is *anomalous*. It is easy to show that the observed rotations agree with the calculations based on the hypothesis that the racemic acid does not exist in solution: Let p and q ($p > q$) be the proportions of the dextro- and lævo-acids in 100 g. of a solution of density d; the total acid concentration is $C = (p + q)d$.

First Hypothesis.—The dextro-acid and the lævo-acid co-exist in the solu-

tion, each acid intervening with that rotatory power which corresponds to its own proper concentration:

$$[\alpha] \text{ right} = a - bp \text{ (for some given radiation).}$$
$$[\beta] \text{ left} = a - bq.$$

The rotatory power of the total acid is (by Biot's formula):

$$[\gamma] = \frac{p[\alpha] - q[\beta]}{p+q} = \frac{p-q}{p+q}[a - b(p+q)].$$

and the rotation corresponding to the chosen radiation is $C[\gamma]$ (per dm.).

We could arrive at this result in another way: The total weight of acid is $p+q$. The rotatory power which the dextro-acid should have at this concentration is: $a-(p+q)b$; but our acid is not pure dextro-acid, but an acid which is racemised to the ratio $\frac{p-q}{p+q}$; the rotatory power is therefore $\frac{p-q}{p+q}[a-(p+q)b]$, which is the first-mentioned value.*

For the diluted solution we have:

$$p = 14{\cdot}79,\ q = 7{\cdot}21,\ p+q = 22{\cdot}0.$$

	D.	E.	F.	*e.*
The calculated rotations are	2·20°	2·30°	2·52°	2·47° (anomalous).

Second Hypothesis.—The racemic acid exists in the solution, and its presence does not affect the rotatory power of the dextro-acid.

Total weight of acid $(p+q)$;
Weight of racemic, $2q$;
Excess of dextro-acid, $(p-q)$;

rotatory power of the dextro-acid $[\alpha] = a-(p-q)b$;

rotatory power of the mixture $\frac{(p-q)[\alpha]}{p+q}$;

rotation of the mixture C. $\frac{p-q}{p+q}[a-(p-q)b]$.

The calculation leads to the following values:

	D.	E.	F.	*e.*
Calculated rotations ...	2·33°	2·72°	3·09°	3·23°.

We recognise that the measured rotations concord with those calculated on the first hypothesis. Everything goes on, as if the dextro-acid and the lævo-acid were simply in juxtaposition in the solution, and as if *the racemic acid did not exist.*

It should be noted that the solution investigated would, at 20°, contain 14·42 g. of racemic acid per 100 g. of solution. When this solution was cooled down to 10°, a considerable quantity of this acid crystallised; from this fact of the deposition of the racemic acid crystals we must hence not conclude that the acid exists in the solution.

C. *Mixtures of Dextro-acid and Racemic Acid.*—After it had been established that the racemic acid does not exist in solution, it was interesting

* It will easily be seen that the identity of these two results is due to the linear character of Arndtsen's formula.

to observe how a mixture of dextro-acid and racemic acid would behave. The results of this investigation are here given. The solution had the following composition:

Racemic acid, $C_4H_6O_6 + H_2O$ ...	4·03 g.	$d = 1·099$.
Dextro-acid, $C_4H_6O_6$	2·26 g.	
Water	21·99 g.	

4·03 g. of racemic acid contain 3·60 g. of $C_4H_6O_6$ + 0·43 g. of water. The real composition of the solution is, therefore:

Racemic acid, $C_4H_6O_6$...	3·60 g.
Dextro-acid	2·26 g.
Water	22·42 g.

and the percentages are: racemic acid 12·7, dextro-acid 8·0. Rotation measured in 20 cm.:

578	546	492	426
2·25°	2·49°	2·55°	2·55°

The dispersion is again anomalous.

The calculation yields:

	D.	E.	F.	*c.*
Second hypothesis ...	2·45°	2·86°	3·26°	3·40°
First hypothesis ...	2·16°	2·47°	2·71°	2·68°

The measurements accord with the values calculated on the first hypothesis. Matters pass as if the racemic acid were in the solution, dissociated into its two constituents; the solution thus behaves like a mixture of dextro-acid and lævo-acid.*

Conclusions.

1. Mixtures in unequal proportions of dextro-tartaric acid and lævo-tartaric acid behave, as regards the rotary dispersion, as if the racemic acid did not exist in solution.

2. In mixtures of dextro-acid and racemic acid matters appear as if the racemic acid were dissociated into its two constituents.

We remember that the investigation, by various experimenters, of diverse properties (cryoscopy, specific gravity, electric conductibility, magnetic rotation, etc.) have been made with solutions of equal concentrations of racemic acid and of dextro-acid. It has not been possible to reveal any difference between those solutions. These results are easily explained by my hypothesis. The racemic acid being dissociated, in the solution, into its two constituents, the solution must have the properties of a dextro-acid or a lævo-acid of the same concentration.

* In order to make the calculations on the second hypothesis, we have assumed that the rotatory power of the dextro-acid remains unchanged by the presence of the racemic acid. This fact is not certain, however. There would only be one way for its verification: add dextro-acid and racemic acid. Now, from what we have just seen, the simple addition does not take place.

THE ROTATORY POWER OF TARTARIC ACID.

(Translated from the French.)

A Paper by **Mr. G. Bruhat** (École Normale Supérieure, Paris) on "The Rotatory Power of Tartaric Acid" was read by Dr. H. Borns.

It has been known since Biot* that solutions of tartaric acid show an anomalous rotatory dispersion. The rotatory power for the different lines of the solar spectrum has been measured by Arndtsen† for solutions of different concentrations in water and in mixtures of water and alcohol. These measurements have been resumed for other concentrations and other solvents by Wendell,‡ Lepeschkin,§ Winther,‖ and Ascher.¶ The results obtained show that, for every solution, the rotatory power attains a maximum for a certain wave-length, which depends upon the concentration and the nature of the solvent. For diluted aqueous solutions the maximum lies in the violet, for concentrated solutions in the green; for supersaturated aqueous solutions and for certain alcoholic solutions the maximum lies in the yellow, the rotation vanishes in the blue and becomes negative in the violet: when some benzene is added to the solvent, the rotation is negative for all wave-lengths.

The tartaric acid hence shows an altogether anomalous variation of the rotatory power, not only as to wave-length, but also as to the concentration and the nature of the solvent. The temperature variation is, further, much stronger than with most active substances, and the rise of temperature modifies the rotatory dispersion curves in the same way as the dilution.

Researches which I have made as to the anomalies of the rotatory dispersion in the neighbourhood of an absorption band have induced me to inquire, whether it would not be possible to approach the behaviour of the solutions of tartaric acid from this phenomenon and to explain the anomalies by the influence of an ultra-violet absorption band, although it appeared difficult to account, by this same cause, for the anomalous variations with the concentration, since the absorption bands in general are not sufficiently affected by the dilution to produce variations of this importance. Concentrated solutions of the acid appear, indeed, always yellow, when examined in a tube several decimeters in length; they therefore absorb the more refrangible parts of the spectrum to a certain extent; but my spectrometric study has shown that the absorption, which sets in at the extremity of the visible spectrum and increases in the ultra-violet, does not really become strong before we come to wave-lengths of less than 247 $\mu\mu$. On the other hand, Cotton has proved that the anomaly in the rotatory dispersion, produced by the existence of absorption bands, is accompanied by circular dichroism; this dichroism is maximum for the wave-length for which the rotation vanishes, and the

* Biot, *Mém. Acad. Sciences*, **15**, p. 93; 1838.
† Arndtsen, *Ann. de Chim. et Phys.*, iii., **54**, p. 403; 1858.
‡ Wendell, *Wied. Ann.*, **76**, p. 1152; 1898.
§ Lepeschkin, *Ber. Dtsch. Chem. Ges.*, **32**, p. 1180; 1899.
‖ Winther, *Zschr. Physik. Chem.*, **41**, p. 161; 1902. **45**, p. 331; 1903.
¶ Ascher, *Inaug. Dissert.*, Berlin; 1912.

theory, which I shall elsewhere advance, would suggest that it is then measured by an angle which is approximately double that of the maximum rotation. Now a concentrated solution of tartaric acid in alcohol which, in a polarimeter tube of 30 cm., gave a maximum rotation of 5° 40′ near 550 $\mu\mu$ and no rotation near 425 $\mu\mu$ has not shown any appreciable dichroism (*i.e.*, of more than one minute) for these latter radiations. It is hence impossible to look for the explanation of the anomalies of the rotatory dispersion of tartaric acid in the selective absorption of this acid for the violet or the ultra-violet.

It has also been attempted to account for the variations of the rotatory power with the concentration by the influence of the molecules of the solvent interposed between the active molecules, for instance, by some influence which they might exert on the arrangement and the movements of the atoms in the interior of the active molecule; but we could not, on these grounds, account for the occurrence of an anomaly of the rotatory dispersion in a transparent solution. Further, the theory of Lorentz, developed by Livens* for solutions, leads to a relation between the rotatory power $[\rho]$ and the index of refraction ν of this form:

$$[\rho] = A \cdot (\nu^2 - 1)(\nu^2 + 2)/(\lambda^2 - \lambda_0^2).$$

This formula would not cause us to foresee any anomalous rotatory dispersion since the index ν—which, even for concentrated aqueous solutions of tartaric acid, does not differ by 1/20 from the index of water—does not undergo any very pronouncedly anomalous variations. Nor does it explain the variation of the rotatory power with the concentration, since the variation of the rotatory power for the D line decreases with the concentration, whilst the index for this same line increases.† The assumption of a purely physical effect of the solvent will not explain the anomalies of the variations of the rotatory power of the tartaric acid therefore.

We are thus induced to assume that there exist in solutions of tartaric acid two active compounds endowed with rotations in the opposite sense and of different rotatory dispersions, whose relative proportions depend upon the nature of the solvent, on the concentration, and the temperature. The hypothesis permits of explaining at the same time the anomalies of the variations of the rotatory power with those three factors and the anomalies of the dispersion. By an analogous phenomenon Darmois‡ has explained the variability of the rotatory power of essences of turpentine and the anomalous rotatory dispersion shown by certain of these essences; the dispersion curves which he gives for mixtures of the two pinenes are entirely analogous to those found for solutions of tartaric acid. He points out that in the case of such mixtures containing two active substances, the rotatory powers α_1, α_2, α_3, β_1, β_2, β_3, given by three different solutions for two monochromatic radiations should satisfy the equation

$$\frac{\alpha_3 - \alpha_1}{\alpha_2 - \alpha_1} = \frac{\beta_3 - \beta_1}{\beta_2 - \beta_1}.$$

In the case of aqueous solutions of tartaric acid this relation is well supported by the experiments of Arndtsen, who was led to suggest that for each radiation the rotatory power was connected with the quantity of water c by a linear function:

$$\alpha = A + Bc$$
$$\beta = A' + B'c.$$

* Livens, *Phil. Mag.*, vi., **25**, p. 817; 1913.
† Cheneveau, *Recueil de Constantes Soc. Franc. de Phys.*, p. 474.
‡ Darmois, *Ann. de Chim. et Phys.*, viii., **22**, p. 247; 1911.

The formula is likewise confirmed by the experiments of Wendell, which also suggest a linear relation, and by the measurements made by Winther, who found that the ratios $(\beta_2 - \beta_1)/(\alpha_2 - \alpha_1)$ (Lösungs-dispersions koeffizient) were independent of the concentrations and had further the same value for alcoholic solutions. He observed, moreover, that the analogous ratios for the same solution at two different temperatures $(\beta_t' - \beta_t)/(\alpha_t' - \alpha_t)$ (Dispersions koeffizient) are constant and essentially equal to the preceding ratios—which proves that one may explain the strong variation of the rotatory power with temperature by the variation of the proportions of the two active compounds.

The hypothesis of two active compounds in equilibrium with one another in variable proportions hence well accounts for the anomaly of the rotatory dispersion and its variation with concentration and temperature. It likewise accounts for the variation with the nature of the solvent; it is, however, difficult to obtain numerical values for solvents except alcohol, the solubility of the tartaric acid being in general too small to admit of precise measurements of the rotation. We can at any rate say that the general trend of the curves is the same as that of the curves given by alcoholic or aqueous solutions, or solutions extrapolated from the former according to the rule of Darmois.

Which is the nature of these two compounds? It is impossible to suggest any intervention of electrolytic dissociation. The cryometric measurements and the conductibility determinations are in accord and show that this dissociation only becomes appreciable for solutions which are too diluted to admit of taking rotatory power measurements. We should then have to suppose that the very small number of ions which exist possess a very high rotatory power, which is not confirmed by the results observed with neutral tartrates, in the case of which dissociation really does intervene.

Biot * had thought that the phenomena he observed were due to a combination between the tartaric acid and water. This assumption does not render clear why the same phenomena are observed with solvents other than water. We can show that this assumption must be rejected by studying the rotatory dispersion of pure tartaric acid in the absence of any solvent. Biot had been able to obtain transparent masses of superfused tartaric acid, and had observed positive rotations for the red rays and negative rotations for blue rays; at a temperature of 3·5° C. he even succeeded in obtaining negative rotations for red rays. I have taken these experiments up again, and I have made my measurements with some precision.

The crystallised tartaric acid is placed in a tube, 5 cm. long and 2 cm. in diameter, which can be heated up to 180° C. in an electric furnace. The tube is placed in a beam of an electric arc between two Glazebrook prisms; the tube is directed with the aid of a finder lens which also converges the luminous rays on the ring (eyepiece). The acid melts when heated to 180° and begins to boil; the light then reappears in the field which is crossed by bubbles. When the analyser is turned, beautiful colours of normal dispersions are seen; the light which passes is green for an azimuth of + 8°, red for an azimuth of + 15°, and shows the transition tint at + 11°. When we stop heating and watch the rotatory dispersion during the cooling period, we observe analogous colours down to temperatures of about 90° C., yet with that difference that all the azimuths are becoming smaller: at 90° C. the azimuth of the transition tint is + 9°. When the temperature continues to fall, the colours, while remaining in the same sequence, become less and less intense, and the azimuths decrease further, that of the transition tint being + 6·5° at 50° C. At about 45° C. we no longer see any blue nor red. We notice a lilac

* Biot, *Ann. de Chim. et Phys.*, iii., **28**, p. 351; 1850.

tint, intense particularly near 4·5°, and brilliant yellow for the lower azimuths. Afterwards, the temperature still falling, the yellow turns into orange and then into red, whilst the azimuth becomes negative ; the azimuth of the lilac tint also diminishes, being 0 or 1° for ordinary temperature, whilst for all the higher azimuths the colouring appears blue. We thus recognise that tartaric acid possesses, when liquid at 180° C., a normal rotatory dispersion, and that the dispersion diminishes at lower temperatures, particularly below 100° C. ; about 45° C. the rotation is maximum for the yellow, and at ordinary temperature it decreases in algebraical value from the red to the violet, vanishing in the middle of the visible spectrum.

It is rather difficult to obtain exact measurements of the rotation for the different colours of the spectrum. When the acid is fused and maintained liquid about 180° C., bubbles are being liberated which agitate the liquid by convection currents, and give rise to a partial depolarisation of the light ; this bubbling is moreover accompanied by a chemical change of the fused material, and we have to operate quickly. On cooling almost all the bubbles congregate near the surface while the acid is still viscous ; crystalline particles may, however, remain in suspension, and the acid may undergo a more or less irregular temper when we pass from the solidification temperature to the ordinary temperature. It may even occur, when we try to cool below ordinary temperature, that fissures form in the mass of acid owing to the unequal dilatation of the acid and of the tube in which it is contained. The fissures render polarimetric observation impossible. Attempts made to anneal the mass have never succeeded ; for a mass of superfused tartaric acid which has been cooled to ordinary temperature crystallises rapidly and throughout the mass as soon as we heat up to 100° C. again. The depolarisation produced by the superfused material and the irregularities of the light rays through this substance make the use of a penumbra-polarimeter impossible. It remains possible, however, to determine the extinction-position in monochromatic light between two Glazebrook prisms ; by focussing the finder on the bubbles or the solid particles, which may be in suspension, the polarised light which they diffuse may be rendered little troublesome.

The tartaric acid was directly fused in the polarimeter tube of 5 cm. length ; the light employed was that of an electric arc purified spectroscopically by the arrangement of Brace* ; the width of the spectrum bands used ranged from 20 to 10 $\mu\mu$. Under these conditions, and taking ten readings of the analyser position at extinction, I found that for the red, yellow, or green radiations these ten readings were distributed over an interval of 45 or 60 minutes ; their mean may therefore be considered as exact within about 10 minutes. I have always verified, when recommencing the measurements after having turned the tube through 90° about its axis, that the temper of the superfused acid did not exert any influence. Yet the different experiments have not yielded entirely identical rotatory dispersion curves ; this is due to the chemical modifications which the tartaric acid undergoes while fusing ; I shall study their effect on the rotatory power.

The results of a few series of observations are given in the following table. Series I concerns a tube containing tartaric acid which was kept fused in an electric furnace, regulated to maintain as constant a temperature as possible ; the temperature would fluctuate between 180 and 185° C. The measurements were taken very quickly so as to avoid chemical decomposition, and each result is the mean of four observations. Series II to V refer to a tube which was observed at different temperatures ; it was placed in an electric thermostat whose temperature was kept steady within ½° C. ; the

* Brace, *Phil. Mag.*, vi., 5, p. 161 ; 1903.

temperatures in these cases were below 100° C., so that alteration of the tartaric acid was not to be feared, and it was possible to wait a sufficiently long time and to allow proper time for careful readings. I have calculated the rotatory power by the ordinary formula, taking the density of the superfused acid at 1·70, which was found by a determination made at ordinary temperature. For the last four series of measurements this density may certainly be accepted; for the solidified acid is glued to the walls of the polarimeter tube and withdrawn from the influence of dilatation. This may not quite hold for Series I, in which the acid was liquid.

I. *Temperature* 180° *to* 185° *C.*

Wave-length ...	...	636	588	547	513	490	447
Rotations observed	...	11° 15′	13° 30′	15° 15′	17°	18°	19° 30′
Rotatory power	...	13·25	15·9	18	20	21·15	22·95

II. *Temperature* 100° *C.*

Wave-length ...	665	630	619	603	584	565	545	534
Rotations observed	7° 48′	8° 10′	8° 32′	8° 57′	9° 16′	9° 37′	10° 8′	10° 27′
Rotatory power ...	9·15	9·60	10·05	10·5	10·9	11·3	11·9	12·25
Wave-length ...	516	512	510	499	490	486	465	447
Rotations observed	10° 58′	10° 58′	10° 59′	11° 19′	11° 17′	11° 9′	11° 4′	10° 54′
Rotatory power ...	12·9	12·9	12·9	13·3	13·25	13·1	13·0	12·8

III. *Temperature* 67·6° *C.*

Wave-length ...	...	681	646	609	583	547	523	507
Rotations observed	...	6° 11′	6° 12′	6° 51′	7°	7° 12′	7° 20′	7° 25′
Rotatory power	...	7·28	7·29	8·06	8·23	8·47	8·61	8·72
Wave-length ...	...	494	494	487	482	468	453	442
Rotations observed	...	7° 18′	7° 28′	7° 6′	7° 9′	6° 52′	6° 2′	4° 57′
Rotatory power	...	8·58	8·78	8·36	8·41	8·07	7·10	5·82

IV. *Temperature* 44·6° *C.*

Wave-length ...	667	664	636	618	602	596	589	576	569
Rotations observed	4° 10′	4° 20′	4° 24′	4° 20′	4° 38′	4° 39′	4° 26′	4° 29′	4° 25′
Rotatory power ...	4·90	5·10	5·18	5·10	5·45	5·47	5·21	5·27	5·17
Wave-length ...	546	535	524	510	510	498	490	462	430
Rotations observed	4° 18′	4° 23′	4° 3′	4° 8′	4°	3° 35′	3° 28′	2° 12′	— 1° 4′
Rotatory power ...	5·06	5·15	4·76	4·84	4·71	4·21	4·07	2·59	— 1·26

V. *Temperature* 15° *C.*

Wave-length ...	679	664	629	613	592	581	571	550	538
Rotations observed	1° 15′	1° 23′	1° 5′	1°	39′	39′	+ 20′	— 14′	— 18′
Rotatory power ...	1·47	1·63	1·27	1·17	0·76	0·76	0·39	— 0·27	— 0·35

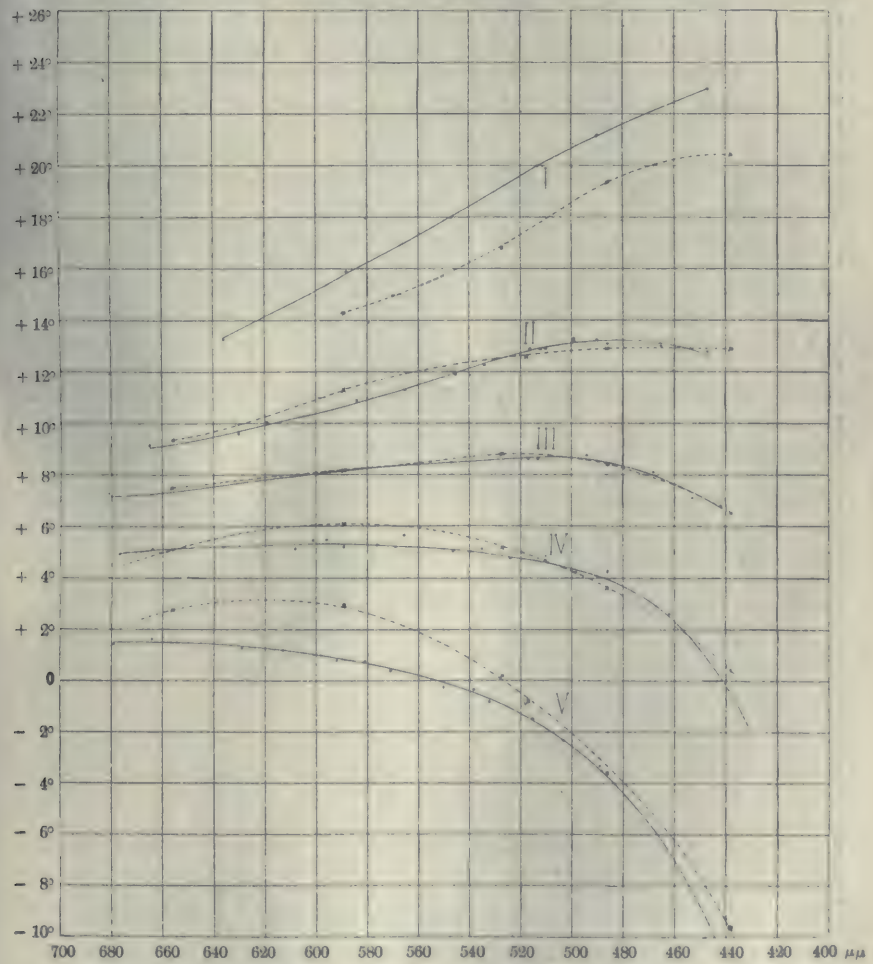
Wave-length—							
532	515	503	489	488	417	455	448
Rotations observed—							
— 43′	— 1° 17′	— 2° 1′	— 2° 55′	— 3° 1′	— 4° 55′	— 6° 12′	— 8° 32′
Rotatory power—							
— 0·85	— 1·51	— 2·36	— 3·33	— 3·55	— 5·79	— 7·30	— 10·05

The drawn-out curves present these results. Their general character has been stated: the dispersion, normal for the liquid acid at 180° C., becomes anomalous below 100° C.; the rotation diminishes for all radiations as

the temperature is lowered, and the maximum rotation is at the same time displaced towards the red. The dotted curves represent the rotatory powers of aqueous and alcoholic solutions as studied by Arndtsen, and further, the rotatory powers of the pure acid extrapolated according to the formulæ of Arndtsen. The analogy of the two systems of curves is striking: *The cause*

ROTATORY POWER OF TARTARIC ACID.

I. Acid fused at 180°. 5 per cent. aqueous solution.
II. Acid superfused at 100°. 30 per cent. aqueous solution.
III. Acid superfused at 67·6°. 50 per cent. aqueous solution.
IV. Acid superfused at 44·6°. Solution in a mixture of water and alcohol.
V. Acid superfused at 15°. Pure acid by extrapolation from aqueous solution.



which produces the anomalous dispersion and its variation, both with the concentration and with the temperature, is the same for the solutions as for the pure acid.

The pure tartaric acid, liquid or superfused, must then contain, like the solutions, the two compounds in equilibrium to which we have ascribed the

explanation of the anomalies. The hypothesis of the formation of hydrates must necessarily be rejected therefore. We might, on the contrary, suppose that the tartaric acid became dehydrated, and that the two compounds in equilibrium were the acid itself and an anhydride; but we could not then explain why the displacement of this equilibrium takes place in the same sense—corresponding to an increase in rotatory power—when we dilute the tartaric acid solution in water or in some other solvent (ethyl or methylalcohol, acetone, acetic acid) and when we raise the temperature of the fused acid. It will hence be advisable to reject this hypothesis as well.

The second compound which exists in the solutions or in the superfused mass can hence only be a complex compound, which is formed by the grouping of several molecules of tartaric acid. This compound will be destroyed by the dilution, in any solvent whatever, or by the elevation of the temperature; these two factors will thus act in the same sense and produce simple tartaric acid, whose rotatory power would be to the right, whilst that of the complex would be to the left and would increase the rotations. The rotations would, on the other hand, be diminished and might be made negative, as experiments indicate, by the addition to the solution of substances like benzene and its homologues which possess the well-known property of favouring polymerisation.

We may attempt to demonstrate the existence of such complex compounds by methods which enable us to determine the molecular mass of the bodies in solution. Aignan * believed to have proved, by determining the osmotic pressure of a solution of 5 per cent., the existence of a compound $(C_4H_6O_6)_2$; but his measurements do not inspire much confidence, and it appears safer to have recourse to freezing-point determinations. We know from Raoult that the diluted aqueous solutions of tartaric acid show normal depressions at the congelation points. I have taken up these experiments again, and I have followed them up to concentration of 70 g. of acid in 100 g. of water. Deviations from Raoult's law did not appear before the concentration exceeded 25 per cent., and these deviations were not in the expected sense, and must be ascribed merely to the insufficiency of Raoult's law for concentrated solutions. Solutions of tartaric acid in acetic acid also follow Raoult's law up to 2 per cent., and they do not deviate from it at higher concentrations more than solutions of other substances do.

We must then assume that, in aqueous solutions of 25 per cent., as well as in solutions in acetic acid of 2 per cent., all of which present a very marked anomaly in the rotatory dispersion with a maximum rotation in the blue or violet of the spectrum, the proportion of polymerised tartaric acid is very small and does not exceed 2 or 3 per cent. If we accepted this value, we might—the rotatory power of the non-polymerised tartaric acid being known, which is that observed in solutions at infinite dilution—calculate the rotatory power of the complex; we should then find values which vary from the line C to the line F, between about $-80°$ and $-200°$. The high order of these figures has nothing extraordinary, when we suppose that we have to deal with molecular complexes which owe their rotatory power to the arrangement of the molecules, like the crystals. The values thus calculated for the rotatory power of the pure tartaric acid and of the molecular complex, the existence of which would give rise to the various anomalies, are altogether comparable to the values shown by the rubidium tartrate, whose rotatory power in solution is $+25{\cdot}63°$, and in the crystallised state $-388°$ (for the D line, along the optical axis). We might also compare these values with the still larger figures for the rotatory power of certain liquid crystals.

* *Ann. de Chim. et Phys.*, vii., 1, p. 433; 1894.

THE CONSTITUTION OF LIQUID MIXTURES AND THEIR ROTATORY POWER.

(Translated from the French.)

A Paper by **Professor A. Cotton** (Paris, École Normale Supérieure) on "The Constitution of Liquid Mixtures and their Rotatory Power" was read by Dr. H. Borns.

One of the most important questions of physical chemistry may be expressed in this form: "What is there in a *mixture* of two pure liquids? What is there in a solution of a pure substance?" The case of the mixture is the simpler of the two, because we can first study the two separate constituents in the same physical state. Although the remarks which I wish to offer will also be useful for the case of solutions, I shall in the following lines confine myself to an examination of mixtures of two pure liquids.

The considerations which H. Mouton and myself have already exposed in a paper on the "Magnetic Birefraction of Mixtures"* are based on the following principle: When we desire to study the problem of the constitution of mixtures by some physical process, the simplest way is to study a property which one of the constituents does not possess; or in other words, to investigate cases for which "inactive" diluents are known. When we inquire into properties such as the refractive index, the magnetic rotatory power, vapour tension, etc., this simplification does not present itself. In order to calculate the properties of the mixture we have to take into account all the constituents which enter into the mixture. On the other hand, the natural rotatory power is only observed when certain elements of symmetry (planes of symmetry, centre of symmetry, planes of alternating symmetry) are wanting in the molecule taken as a whole. In this case there are inactive diluents. There exist also inactive diluents when we investigate the magnetic birefraction: examined with the aid of the means actually at our disposal at least, the magnetic birefraction of carbon tetrachloride CCl_4 is nil, *e.g.*, whilst a great number of compounds, particularly the aromatic compounds, show a decided magnetic birefraction. This birefraction also depends upon the structure of the molecule, upon its anisotropy.

Let us consider the natural rotatory power, for instance. We mix two liquids, an active liquid A, and another A′ which does not act upon polarized light. In order to simplify the exposition I will assume that we effect the mixing in the polarimeter tube itself, whose cross-section be constant (of unit value) whilst the length may be varied. We effect the mixing by putting into the tube a mass c of the active substance A, and another quantity—which it is not necessary to designate by a letter—of the inactive liquid A′. The simplest case that can arise is that of simple additivity. The measured rotation R will only depend upon the mass of the active liquid, and we shall have $R = rc$, where r designates the rotation which we observed when we put unit mass of A into the tube.

* *Ann. de Chim. et Phys.*, **30**, p. 321, November, 1912.

This case is exceptional; in most instances this law of additivity will not hold. Everybody knows that the specific rotatory power changes in general when we change the diluent. It is these variations which we have to explain.

Two theories present themselves. On the *physical* theory we admit that each molecule of the active substance A rests such as it was, but that the action which it exerts is modified by the presence of the molecules of A'. This first way of approaching the problem is closely connected with the ideas of Van der Waals and his school. We remember that a large number of papers have been published in the Netherlands during these last years on liquid mixtures. The consideration of the mutual actions plays a preponderating part in these researches with respect to the explanation of experimental facts concerning the equation of state, the miscibility of liquids, the viscosity, vapour tension, refractive index, etc.

In the theory which may be called *chemical* we assume that there are present in the mixture not only molecules of A and molecules of A', but also complexes. It is assumed that mixed complex compounds AA' are formed in a proportion which varies with the concentration, or that one of the pure liquids, A, *e.g.*, contains molecular associations AA whose dilution produces a variation in the proportion. The associations or complexes exist in the mixture by the side of molecules of A and A'. The characteristic feature of this theory is that the associations or mixed complexes which we suppose to exist have a definite composition: they are defined in the state of known components; such are, for instance, the hydrates of a salt. This chemical theory has in particular been advocated by Dolezalek.* In certain cases it represents the real experimental facts in a remarkable way; Dolezalek and A. Schulze certainly explain, for instance, the properties of mixtures of ether and chloroform by a combination of molecule and molecule of the two substances present, a combination which they have, moreover, succeeded in obtaining in the solid state and which has a definite melting-point. But this is a case of a mixture, whose properties deviate considerably from those which the laws of additivity would lead us to predict; the combination, moreover, is accompanied by a sensible contraction. Are we entitled to extend this theory to cases of mixtures not accompanied by any measurable contraction?

Experiments should enable us to answer this question in certain cases, and to demonstrate whether this chemical theory is by itself sufficient to explain the properties of mixtures. We can employ two distinct methods: (1) Measure the rotatory power (or the magnetic birefraction) for diverse radiations; (2) Measure at the same time the rotatory power and the magnetic birefraction.

1. *Application of Several Radiations.*—This is the method of Darmois.† I shall generalise his remarks a little; what I am going to say will apply, exactly and without modification, to the magnetic birefraction and to any other property which one of the constituents of the mixture possesses in the pure state. I presume, as previously, that we effect the mixing in a polarimeter tube of variable length and of constant cross section, into which we have put a mass c of the active body A and another quantity of the inactive body A'. Let us suppose that a mixed complex AA' is formed. The total mass c of the active substance consists of two portions; the one portion μ may be bound in the state of a complex AA', the other $(c - \mu)$ may remain in the primitive state, that is to say, it is still pure A. Let R signify the rotatory power of the

* *Zeitschr. Physik. Chem.*, **69**, p. 727 (1908); **71**, p. 191 (1910); **73**, p. 45 (1913).

† Darmois, *Thèse de Doctorat.* Paris, 1910. *Ann. de Chim. et Phys.*, **22**, pp. 247 and 495, 1912.

mixture, r the rotatory power which would be found if we placed unit mass of A into the tube of variable length, and ρ the rotation which would be observed if we could isolate the complex AA′ and place in the same tube this pure complex, containing the unit mass A.

Then—

$$R = r(c - \mu) + \rho\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a relation in which two unknown quantities μ and ρ occur. Measurements made with the aid of a single wave-length cannot suffice to give any information as to the constitution of the mixture. (It would at least be necessary to have recourse to other considerations, such as the law of mass action.) But it is different when we conduct the measurement for *several* simple radiations. Let λ_1 be the wave-length of such a radiation ; the corresponding other values would be R_1, r_1, ρ_1, and similarly λ_2 would correspond to R_2, r_2, ρ_2. We shall have—

$$R_1 = r_1(c - \mu) + \rho_1\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$R_2 = r_2(c - \mu) + \rho_2\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and after eliminating μ—

$$\frac{R_1 - cr_1}{R_2 - cr_2} = \frac{\rho_1 - r_1}{\rho_2 - r_2} = C_{1,2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$C_{1,2}$ being a constant which is the same for all the mixtures of diverse concentrations because it merely depends upon the specific properties relative to the wave-lengths λ_1 and λ_2 of the pure body and of the complex. The verification of the constancy of this ratio, or of the analogous ratios $C_{1,2}$ . . ., which we can determine by making use of other radiations, will show whether the chemical theory is sufficient. It must be understood that for this verification we have to bear in mind that in practice the experiments are not made with a tube of variable length. We can easily calculate the coefficients by which we have to multiply the measured value in order to find the quantities which enter into the first term of equation (4).

This verification may be by a graphical method. We should construct, for each radiation applied, two curves Γ and R, whose abscissæ represent the compositions of the mixtures under examination (concentration by volume of the substance A, contents by weight, etc.). The ordinates would be for Γ the calculated values cr, c being known from the composition of the mixture, and for R the measured values of R which correspond to the same value of c. The differences of the ordinates of the two curves $\Gamma_1 - R_1$ with regard to one radiation would then be proportional to the differences of the ordinates $\Gamma_2 - R_2$ with regard to another wave-length. (Since we are to a large extent masters of the determination of the abscissæ and of the values of c, we need only make them proportional in order that the curves Γ be straight lines.)

The measurement of the rotatory power (or of the magnetic birefraction) would then, when taken with wave-lengths from different parts of the spectrum, furnish a first means of submitting the chemical theory to an experimental test. I have so far assumed that a mixed coupler AA′ be formed. We should have arrived at the same result if the molecules of A were merely associated with one another. If the rule as stated be confirmed, we may assert that in the mixtures studied there are two active constituents and only two ; the rule would not afford any clue as to the nature of these constituents.

2. *Simultaneous Measurement of the Rotatory Power and of the Magnetic Birefraction.*—The method which Mouton and myself have proposed for the control of the chemical theory would in certain cases allow us to go farther. The method consists in determining, in the same mixture and for a single radiation, both the rotatory power and the magnetic birefraction. It will be easy for us to apply this method as soon as we shall have an electro-magnet at our disposal which is bigger than our actual electro-magnet. I will not, on this occasion, describe how this method is applied.

There are two kinds of mixtures whose study would be interesting. In the first instance we have a body A which possesses both rotatory power and magnetic birefraction; we add to this substance another A′ which is inactive in both these respects. In the second instance we mix a body A, which possesses only rotatory power, with a body A′ which possesses only magnetic birefraction.

First Case.—Reasoning as before and assuming the formation of the complex AA′ we have again the relation derived from the consideration of the rotatory power for a certain radiation: $R = r(c - \mu) + \rho\mu$ . . . (1) and another relation, altogether analogous, derived from the consideration of the magnetic birefraction for a certain radiation (the same radiation as before or not):

$$B = b(c - \mu) + \beta\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where c and μ retain their meaning and where B, b, β are the birefractions defined in the same way as R, r, ρ.

With regard to these two equations (1) and (5) we can argue exactly as we did with regard to (2) and (3). If the chemical theory be correct, we must confirm for mixtures of diverse concentrations the relation

$$\frac{R - cr}{B - cb} = C \text{ constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Again, we should arrive at the same relation if we assumed that associations AA were formed; that is to say that, in this case as before, we are unable to distinguish between mixed complexes and the state of association of A modified by the diluent.

Second Case.—Let us assume that A alone possesses rotatory power, and that A′ alone possesses magnetic birefraction. When we place into the tube the unit mass of A, we measure the specific rotation r. When we place the unit mass of A′ into the tube, we shall measure the specific birefraction of this substance, which I will designate by b'. Let, further, ρ and β be the rotatory power and the magnetic birefraction with regard to the unit mass of the complex AA′, whose formation we presume; let c and c' be the masses of the two bodies which are mixed in the tube, and finally μ and μ' be the masses of the two substances which are present in the mixture in the state of the complex AA′. We shall then have—

$$R = r(c - \mu) + \rho\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$
$$B = b'(c' - \mu') + \beta\mu' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

from which we deduce—

$$\frac{R - rc}{B - bc} = \frac{\mu}{\mu} \cdot \frac{\rho - r}{\beta - b'} = C \text{ constant} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The ratio μ/μ' of the masses of the two bodies which form a definite complex is evidently constant indeed, and the four quantities ρ, r β, b' only

depend upon the specific properties of the complexes and of the pure bodies. The measurements and the verifications are made as before.

When no mixed complexes are formed, and when there is modification merely by the dilution of a number of associations formed between the molecules of *one* of the constituents, it will only be the phenomenon, for which this constituent is active, which will not obey the law of additivity. When we have, for instance, in the mixture molecules of A, molecules of A′, and associations A′A′ we shall find

$$R = rc\,;\ B \neq b'c',$$

and conversely—

$$R \neq rc\,;\ B = b'c',$$

when the associations AA are present in the mixture. This second case thus yields more complete information. We see, therefore, that the determination of the rotatory power, combined with the determination of the magnetic birefraction, helps us to solve the question: What happens when we mix two liquids? These determinations will indicate whether the chemical theory affords a *sufficient* explanation of the experimental facts.

SIMPLE AND COMPLEX ROTATORY DISPERSION.

Dr. T. Martin Lowry and **Mr. T. W. Dickson** read a Paper on "Simple and Complex Rotatory Dispersion."

The object of the present paper is to discuss the form of the curves of rotatory dispersion in the light of experimental evidence obtained in a series of recent investigations. Some of these have already been published,* whilst others are still awaiting completion. The experiments cover all the different varieties of optical rotation, namely: (1) the natural rotations observed in crystals of quartz, and (2) the artificial rotatory power produced by placing quartz in a magnetic field, (3) and (4) the optical and magnetic rotations in optically-active liquids such as *sec*-butyl alcohol and its homologues. The experiments include observations in the ultra-violet and infra-red, as well as in the visible region of the spectrum.

A.—*Rotatory Dispersion in Quartz.*

The only data which will permit a *rigid* test of the form of the curve of rotatory dispersion are those which have been obtained in the case of quartz. Whereas, in the case of other substances, it is very rarely practicable to obtain readings as large as 100°, it has been found possible in the case of quartz to record an *observed* rotation exceeding 100,000°. In the visible region of the spectrum, readings can be taken to seven significant figures, with errors of observation amounting to only a few parts per million. The readings can be extended into the ultra-violet, at least as far as wave-length 2,200 A.U., and at least as far as wave-length 20,000 A.U. in the infra-red. In the ultra-violet the readings can be taken without difficulty to 1°, and it would not be difficult, by mere perseverance, to reduce the errors of observation to about 0·1°. As the readings are larger than in the visible spectrum, the errors of observation are, relatively, not much greater; indeed, if attention be paid to the fact that the photographic observations are made on narrow spectrum-lines, whilst the visible readings are taken with wide blocks of light, the greater spectral purity of the ultra-violet readings may impart to them a higher degree of accuracy than that actually attained by visual observation. The infra-red readings are necessarily of a lower order of accuracy, but are of great value on account of the wide range of wave-lengths which they cover.

The first formula for the rotatory dispersion of light in quartz was given by Biot, who suggested that

$$\alpha = \frac{k}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Lowry, *Proc. Roy. Soc.*, 1908, A. **81**, 472–474; *Phil. Trans.*, 1912, A. **212**, 261; *Trans. Chem. Soc.*, 1913, **103**, 1062–1067. Lowry and Dickson, *ibid.* 1067–1075. Lowry, *ibid.* 1322–1331; *Trans. Chem. Soc.*, 1914, **105**, 81–94. Lowry, Pickard and Kenyon, *ibid.* 94–102. Lowry and Dickson, *Proc. Chem. Soc.*, June 5, 1913.

The rotation produced in light of any colour being inversely proportional to the square of the wave-length. Boltzmann gave the equation

$$\alpha = \frac{k_1}{\lambda^2} + \frac{k_2}{\lambda^4} + \frac{k_3}{\lambda^6} + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

corresponding closely with Cauchy's formula for refractive indices. Drude* suggested a general equation

$$\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation, if $\lambda > \lambda_n$, can be expanded into a series of the same type as Boltzmann's equation (2).

In Drude's equation the constants λ_n are the wave-lengths in vacuo of light having the same periods as the free vibrations of the "ions" or "electrons" by which the optical properties of the molecule are determined. In the case of quartz the values of these constants (in microns squared) have been deduced from measurements of refractive power as follows—

$$\lambda_1^2 = 0{\cdot}010627$$
$$\lambda_2^2 = 78{\cdot}22$$
$$\lambda_3^2 = 430{\cdot}6.$$

Drude assumed that these refraction-data could be used to determine the course of the curve of rotatory dispersion. He therefore wrote the equation in the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k_3}{\lambda^2 - \lambda_3^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and calculated the values of k_1, k_2, k_3, etc., from existing data for the rotatory power of quartz over the range from 21,400 A.U. (2·140 microns) to 2193·5 A.U. (0·21935 microns). He found $k_2 = k_3 = 0$, and concluded (i) "*that the kinds of ions whose natural periods lie in the ultra-red are inactive.*" On the other hand, he had already adopted the view that quartz has ions for which λ_n is much smaller than the wave-length of light, and concluded (ii) "*that the activity coefficient k′ of ions of this kind, for which λ_n^2 may be neglected in comparison with λ^2, must be taken into consideration.*" By throwing the equation into the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\lambda_1^2 = 0{\cdot}010627$, $k_1 = 12{\cdot}200$, $k' = -5{\cdot}046$, Drude was able to calculate the rotatory power of quartz over the whole range with an average error of 0·060° per mm. in a series of 18 observations.

The more accurate measurements put forward in 1912 could not be represented, even in the narrow range of the visible spectrum, by Drude's simplified equation (5). In order to secure a reasonable concordance between the observed and calculated values, it was necessary to go back upon Drude's first conclusion and to restore an infra-red term to the equation, which thus became

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This formula gave results which were a great improvement on the figures quoted by Drude, the average discrepancy in the visible region of the spectrum being reduced from 0·038 to 0·001° per mm.

* *Theory of Optics*, 1907, p. 413.

Further measurements in the ultra-violet region, which are not yet available for publication, show that even this improved formula becomes grossly inaccurate when carried out towards the limit of transmission of light by quartz. It cannot be made to give good results so long as the values of λ_1^2 and λ_2^2 as deduced from the refraction data are used as constants in the equation, thus limiting the number of arbitrary constants to three. The value of the infra-red term is not important, since it comes into the equation as a quantity that remains almost constant over a wide range of the spectrum; there is therefore no objection to retaining the value of λ_2^2 deduced from the refractive-power of the crystal in the extreme infra-red. But there is good reason to think that the value of λ_1^2 has been given incorrectly, and that the value of this constant may be deduced with much greater accuracy from exact observations of rotatory dispersion than from measurements of refractive power.

It is impossible at present to state the final form of the equation, but a very satisfactory agreement can be obtained over the whole range from w.l. 16,740 to w.l. 2,327 by using Drude's general equation with *three* terms, namely one infra-red term and two ultra-violet terms, thus—

$$a = \frac{k_0}{\lambda^2 - \lambda_0^2} + \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In this equation $\lambda_2^2 = 78{\cdot}22$ as before; λ_1^2 is a constant differing somewhat from the value 0·010627 given by Drude; λ_0^2 represents another wave-length in a remote part of the inaccessible ultra-violet region. It is not negligible, as Drude supposed, but its magnitude is so small that the "probable error" as determined from the incomplete data at present available was found to be larger than the number itself. An equally good agreement can, however, be reached by replacing the whole of the infra-red term by a constant, putting $\lambda_0^2 = 0$, and regarding λ_1^2 as an unknown quantity. The equation then becomes

$$a = \frac{k_0}{\lambda^2} + \frac{k_1}{\lambda_2 - \lambda_1^2} + k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This equation contains four arbitrary constants, as compared with the three arbitrary constants of equation (6) and the five arbitrary constants of equation (7). This number of constants appears to be quite sufficient to express the data at present available, and, from the empirical point of view, affords the most satisfactory solution of the problem of reducing the data to algebraic form.

B.—*Optical and Magnetic Rotatory Dispersion in Simple Organic Liquids.*

In the case of a large number of simple organic liquids, the optical and magnetic rotatory dispersion may be expressed by the equation

$$a = \frac{k}{\lambda^2 - \lambda_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Thus the average values of the *magnetic* dispersion-ratios in a series of 25 substances have been found to compare with the calculated values as follows:

	Li	Cd	Na	Hg	Cd	Cd	Hg
	6,708.	6,438.	5,893.	5,461.	5,086.	4,800.	4,359
Obs.	0·647	0·705	0·850	1·000	1·164	1·321	1·636
Calc.	0·647	0·705	0·850	1·000	1·166	1·322	1·636

In the case of the *optical* rotatory power of phenylmethylcarbinol, $C_6H_5.CH(OH).CH_3$, the figures are:

Obs.	0·629	0·687	0·839	1·000	1·184	1·361	1·736
Calc.	0·627	0·687	0·839	1·000	1·183	1·362	1·735

These figures show that the simple formula is sufficient to express the course of the curves of optical and magnetic rotatory dispersion within the limits of the visible spectrum.*

This does not prove that the substances in question are characterised by only one natural period of free vibration. Even in the case of quartz, which is known to possess four such natural periods, the optical rotatory power can be represented *within the same limits of accuracy* by the simple formula But, until the methods of measurements have been developed to an extent which is now quite impracticable, the simple formula will hold its own, as the only possible way of expressing the experimental data in the case of simple organic liquids.

C.—*Anomalous Rotatory Dispersion in Ethyl Tartrate.*

The following data are taken from an early series of observations on ethyl tartrate, but have not been published previously. The rotations shown are the actual readings for a 6 dm. column of the tartrate at 20° C. A much more detailed examination of the form of the dispersion curves for this ester is in progress, but the figures now put forward are sufficiently exact to show that

TABLE I.—*Anomalous Rotatory Dispersion in Ethyl Tartrate.*

$$\delta = \frac{132{\cdot}78}{\lambda^2 - {\cdot}026} - \frac{103{\cdot}05}{\lambda^2 - {\cdot}061}$$

		Observed.	Calculated.	Calc.–Obs.
Cd red	6,708	50·06°	50·26°	+0·20
Zn red	6,364	51·03	50·78	−0·25
Na yellow	5,893	53·32	53·32	±
Cu yellow	5,782	53·60	53·63	+0·03
Hg yellow	5,780	53·69	53·63	−0·06
Cu yellow	5,700	53·58	53·74	+0·16
Hg green	5,461	53·42	53·36	−0·06
Cu green	5,219	51·49	51·41	−0·08
Cu green	5,154	50·62	50·50	−0·12
Cu green	5,105	49·53	49·72	+0·19
Cd green	5,086	49·44	49·35	−0·09
Cd blue	4,678	35·64	35·69	+0·05
Hg violet	4,359	10·79	10·76	−0·03
Photographic observations :—				
	4,737	40	39	−1
	4,443	20	19	−1
	4,250	0	−3	−3
	4,133	−20	−22	−2
	4,034	−40	−42	−2

* Additional evidence in reference to the optical rotatory power of α-methyl-glucoside is given in the following paper (Lowry and Abram, p. 105).

these more complex curves can be represented by a Drude formula containing two terms of opposite sign. The photographic data are taken from some of the earliest observations made by this method and have no claim to be exact; but they have the merit of showing that, as the limit of the visible spectrum is approached, the rotation changes in sign and the ester becomes strongly lævo-rotatory*; moreover, the curve, as thus greatly extended, adheres closely to the course marked out for it by measurements made in the region in which visual observations can be taken.

It should be noticed that the formula given above can be interpreted in a variety of ways. The two free periods are both beyond the limits of observation, and the anomaly is therefore not due to Cotton's phenomenon. But the form which the equation takes might be due (i) to two vibrations of unequal period and opposite activity, as suggested by R. W. Wood; (ii) to the superposition of two "partial-rotations," as investigated by Tschugaeff in the case of menthyl camphor-β-sulphonate; or (iii) to the actual presence of two distinct substances, as in the mixtures of turpentine and camphor, which were shown by Biot to give rise to anomalous rotatory dispersion.

D.—*Dynamic Isomerism as a Cause of Anomalous Rotatory Dispersion.*

Whilst there is no reason to doubt that anomalous rotatory dispersion (especially in compounds containing several asymmetric carbon atoms) may be due to the superposition of partial rotations of opposite sign, there is good reason to think that this phenomenon is more commonly produced by the presence of two or more different compounds in a liquid which nominally contains only one optically-active constituent. This view was expressed by Arndtsen, in 1858, as a means of interpreting his observations on the anomalous rotatory dispersion in solutions of tartaric acid. After quoting Biot's experiments on the anomalous rotatory dispersion in mixtures of turpentine and camphor, he writes:

"One might then regard tartaric acid as a mixture of two substances differing only as regards their optical properties, of which one had a negative rotatory power, the other a positive rotatory power, these rotations varying in different proportions with the refrangibility of the light." †

Two modifications of a substance, differing in their optical properties but identical in chemical behaviour, may be produced—

(i) By association with the solvent;
(ii) By polymerisation of the solute; or
(iii) By isomeric change.

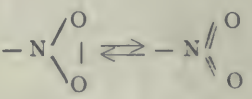
In order that the chemical properties of the two modifications may be the same, it is necessary that these changes should be reversible; if this condition is not fulfilled, the two modifications could be separated by ordinary methods of fractionation, and the liquid would differ in no essential point from Biot's artificial mixtures of dextro- and lævo-rotatory compounds.

The way in which a homogeneous solid may give rise to a mixture on fusion or dissolution may be illustrated most readily in the case of the reversible isomeric changes, which have been very fully studied under the name of *dynamic isomerism*. It has been shown, for instance, that nitrocamphor changes over in solution (to the extent of about one-sixth) into an acidic isomeride, of opposite rotatory power and probably of unequal

* The lævo-rotation has been traced since as far as − 83°.
† *Ann. Chim. Phys.*, 1858, **54**, 421.

dispersive power, thus giving rise to just the right conditions for anomalous rotatory dispersion. The anomaly would here be due to a chemical change belonging to type (iii) *reversible isomeric change*. All the phenomena would be the same if one of the modifications existed, *e.g.* in a bimolecular form as $[C_{10}H_{15}NO_3]_2$,* but the anomaly could then be attributed to (ii) *reversible polymeric change*. Further, one of the modifications might combine with the solvent† ; in this case the phenomena would be precisely similar, but the anomaly might be classified as due to a change of type (i) *association with the solvent*.

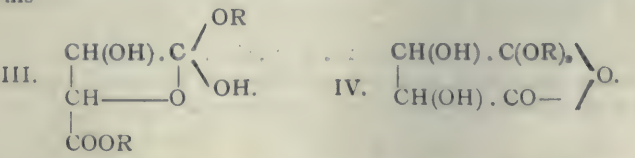
In the case of nitrocamphor, isomeric change in solution is sufficiently slow to give rise to the phenomenon of *mutarotation*, and it was by observations of this kind that the change was first detected. But it is to be expected that anomalous rotatory dispersion may reveal many reversible changes which reach a condition of equilibrium too quickly to be detected or studied by dynamic methods. In the discussion on Pickard and Kenyon's paper,‡ it was suggested by one of us (T. M. L.) that a change of type such as that involved in the conversion of tervalent into pentavalent nitrogen—



might be demonstrated by observations of anomalous rotatory dispersion in an optically-active nitro-compound, even if too elusive to be detected by any other method. So also an elusive polymerisation may reveal itself by producing anomalous rotatory dispersion in an active liquid, just as the polymerisation of nitrogen dioxide $2NO_2 \rightleftarrows N_2O_4$ manifests itself in the varying colour of the gas or liquid, although the changes are too rapid to admit of the separation of the two components by ordinary methods.

In the special case of the tartrates, Armstrong and Walker§ have suggested four formulæ for the isodynamic forms of the acid. In the tartaric esters, two of these modifications might appear as dynamic isomerides—

but the third would probably decompose into an alcohol and an acid-ester, whilst the fourth would be a stable isomeride, not readily convertible into the other forms—



As a matter of fact, ethyl tartrate appears to be a commonplace mixture, which can be fractionated by ordinary methods into portions which differ widely in their rotatory power for violet light ; it may therefore contain

* The acidic form of nitrocamphor might be expected to polymerise in non-ionising solvents, compare acetic acid in benzene $[C_2H_4O_2]_2$.

† There is good reason for thinking that normal nitrocamphor forms unstable compounds when dissolved in benzene and its homologues.

‡ *Proc. Chem. Soc.*, Nov. 20, 1913.

§ *Proc. Roy. Soc.*, 1913, A. 88, p. 399.

the fixed ester IV. in addition to various labile forms of the ester I. But methyl tartrate, which is a well-defined crystalline compound and resists fractionation, also shows anomalous dispersion; this cannot be attributed to ordinary static isomerism, but may be due to a dynamic isomerism of one of the more elusive types, in which the change of structure is too rapid to manifest itself by mutarotation in the freshly-prepared solutions. Some such labile isomerism, involving little more than a re-arrangement of residual affinities, must also be postulated to account for the anomalous rotatory dispersion in the simple esters described by Pickard and Kenyon. Even more emphatically are the coarser types of isomerism ruled out in the case of naphthylmethylcarbinol, $C_{10}H_7 . CH(OH) . CH_3$, the anomalous dispersion in which (if not due to polymerisation) may perhaps depend on the concrete existence of two or more of the many varieties of the aromatic nucleus postulated by organic chemists during the past 50 years.

E.—*Simple and Complex Rotatory Dispersion.*

In the preceding pages it has been shown that every case of rotatory dispersion that has been investigated can be represented by means of Drude's equation. Instead of making a distinction between "normal" and "anomalous dispersion," it would be more satisfactory at the present time to distinguish in the first place between *simple rotatory dispersion*, which can be expressed by the equation

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

and *complex rotatory dispersion*, which must be expressed by an equation containing two or more terms, thus:

$$\alpha = \frac{k_1}{\lambda^2 + \lambda_1^2} + \frac{k_2}{\lambda^2 + \lambda_2^2} + \ldots$$

A complex rotatory dispersion may become "anomalous," as R. W. Wood has pointed out, whenever the range of observations covers the region between two absorption bands. This statement includes the anomalous dispersion of Cotton's phenomenon, where the anomaly is observed in the region between an accessible absorption band and an inaccessible band in the remote ultra-violet.

A second form of anomalous dispersion may be produced by two bands on the ultra-violet side of the region under observation, provided that these are associated with rotations of opposite sign. This anomaly is only to be looked for in the case of optical rotations, since negative magnetic rotations are confined to a small range of metallic compounds and have never been detected in optically-active organic compounds.

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AN ENCLOSED CADMIUM ARC FOR USE WITH THE POLARIMETER.

Dr. T. Martin Lowry and **Mr. H. H. Abram** described and exhibited "An Enclosed Cadmium Arc for Use with the Polarimeter."

It is no longer necessary at the present time to emphasise the importance of rotatory dispersion, *i.e.* of measuring rotatory powers for a whole range of wave-lengths, instead of recording only one point on an unknown curve. But as regards methods of measurement, the necessity of using pure monochromatic light may still be urged. Light filters must be regarded as suited only for a first approximation, since the optical mass centre of the transmitted light may vary with the source of light, and in any case it is impossible to get exact readings of big rotations, which no longer give an extinction. Spectral purification of white light is better, but the "monochromatic illuminator" requires careful use to be sure that the wave-length used is actually that recorded on the drum of the instrument.

In the early days of the measurement of rotatory dispersion it was necessary to use a large range of wave-lengths, as the form of the curve was quite unknown. Thus, in 1908, measurements of the rotatory power of methyl camphorcarboxylate were given for 26 wave-lengths, namely :

Li 6708. Na 5893. Tl 5351.
Hg 5790, 5769, 5461, 4359.
Cd 6438, 5086, 4800, 4678.
Ag 5469, 5209. Zn 6364, 4811, 4722, 4680.
Cu 5782, 5700, 5219, 5154, 5105, 4705, 4651, 4587, 4378.

Twenty-four wave-lengths were used in measuring the rotatory power of quartz in the visible region of the spectrum, and readings (as yet unpublished) have been taken by a photographic method for over 700 wave-lengths in the visible and ultra-violet regions of the spectrum.

In the case of substances whose rotatory dispersion is anomalous, it is still desirable to extend the observations to include a large number of wave-lengths, spread out over a wide range of the spectrum. But in the case of substances whose rotatory dispersion is normal, a much smaller range of wave-lengths will suffice : in fact, in the case of all those substances whose rotatory power can be expressed by the simple formula

$$a = \frac{k}{\lambda^2 - \lambda_0^2}$$

only two observations are required in order to determine the two constants of the equation. These two fundamental observations are most conveniently made with the green and violet rays of the mercury spectrum, since the ratio a_{4359}/a_{5461} is something like 10 times more sensitive than, *e.g.*, the ratio

a_{5461}/a_{5893}. The simple apparatus required for measuring this ratio is being exhibited by the courtesy of Messrs. Adam Hilger, who have supplied the polarimetric equipment, and the Westinghouse Cowper-Hewitt Co., who have supplied the mercury-lamp.

It still remains, however, to establish a satisfactory method of proving that the curve of rotatory dispersion is strictly normal. This can be done to a rough approximation by reading one or two additional wave-lengths and then plotting $1/a$ against λ^2, when the whole of the readings should fall upon a straight line. The most convenient readings to take for this purpose are Na 5893 and Li 6708. But the sodium line is too near the mercury-green to reveal any but the grossest anomalies, and the lithium line, which represents the "furthest south" in the direction of the infra-red, cannot be relied on to give readings of the same order of accuracy as in the case of the two mercury lines. The simple formula given above was therefore verified, in the first place, only when the readings for 23 substances of similar dispersive power were averaged in order to eliminate individual errors of observation. It was at this point that the enclosed cadmium arc made its appearance, with the result that it promises to effect a revolution in polarimetric methods comparable with that which has resulted from the introduction of the mercury arc.

The methods by which the cadmium spectrum was first rendered available for accurate polarimetric work in the visible region were shown before the Physical Society in June, 1909, and described in a paper published in the *Proc. Phys. Soc.*, vol. 22, and also in the *Phil. Mag.* of August, 1909. The apparatus consisted of two electrodes of a silver-cadmium alloy, rotating in opposite directions on spindles driven from a small electro-motor. On striking an arc between the electrodes a brilliant spectrum was emitted which included the lines of silver and of cadmium. Apart from the annoyance caused by the flickering of the arc, this apparatus can be used very effectively if the polarimeter is provided with a constant-deviation spectroscope to purify the light before it enters the polariser. But it cannot well be used with the simpler apparatus, in which the light is resolved only by a direct-vision prism on the eye-piece, as the unextinguished parts of the spectrum are usually too dazzling to permit of easy reading of any one line at the extinction-position. The "method of producing an intense cadmium spectrum" by means of a silver-cadmium arc was therefore "not put forward as the ideal way of producing an intense cadmium spectrum, but rather as an intermediate stage in the development of the perfect cadmium lamp of the future." The search for the perfect cadmium lamp has been in progress ever since, and by the generous co-operation of Mr. F. Stanley, of Messrs. Adam Hilger, we are able to exhibit—not perhaps the perfect lamp itself, but one of its more or less distant ancestors in the process of its evolution.

The form of the lamp is shown in Fig. 1. The arc is run between water-cooled electrodes of *solid* cadmium; this is important, partly because it checks the vaporisation of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped. The lamp must be used in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and these must be pumped off in order to maintain the vacuum. Occasionally, when the vacuum is good, the arc will start itself by merely switching on the current, but usually it is necessary to start the arc by a spark; this can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer

walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In our most recent lamp we have tried to protect these windows from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube, which must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica has been provided to bring the arc to the centre of the tube.

The cadmium arc will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight.* The extinction of the lamp on the lower voltages is caused most frequently by the distillation of cadmium from the electrodes, which thus become shortened unduly. We have tried to check this defect by enlarging the diameter of the tubes containing the metal, but have not yet had enough experience to say how far we have been successful in our endeavours.

The cadmium lamp, which is still in the experimental stage and obviously far from perfect, is only just being brought into actual use in our polarimetric work. We can, however, quote one example of the kind of service it may be

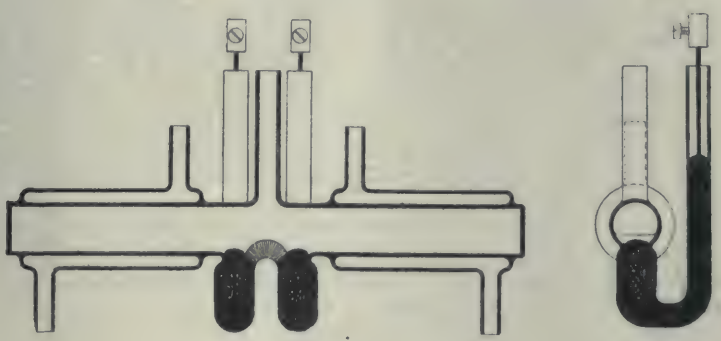

FIG. 1.

expected to render. It was desired to find out in the case of α- and β-methylglucosides, not merely the magnitude of the constants in the dispersion-equation, but also whether these two compounds, containing no less than 5 asymmetric carbon atoms, nevertheless obeyed rigidly the simple dispersion law. Solutions of the two glucosides were made, containing 25 grams in 100 c.c., and these were examined in 600 mm. polarimeter tubes. The readings were as follows :

		α-Methylglucoside.		β-Methylglucoside.	
Mercury	Violet	155·32°	Ratio	33·32°	Ratio
	Green	94·17	1·649	19·95	1·666
Cadmium	Green	109·90	Ratio	23·51	Ratio
	Red	66·10	1·663	14·09	1·669

It will be seen that the ratios for the two cadmium lines are almost equal to the ratios for the two mercury lines. Each pair of lines can be read

* The lamp shown in the figure requires 200 volts : at the meeting, a lamp of simpler pattern was shown burning on a 100-volt circuit.

without disturbing the setting of the apparatus, and the cadmium readings (unlike those for lithium) are quite as reliable as the mercury readings and equally suited for working out the "rotation constant" k, and the "dispersion constant" λ_0^2, for either substance. The values of the constants are :

	k.	λ_0^2.
α-Methylglucoside.		
From mercury readings ...	25·87°	0·0234
From cadmium readings ...	25·85°	0·0235
β-Methylglucoside.		
From mercury readings ...	5·40°	0·0274
From cadmium readings ...	5·48°	0·0257

The figures for the α-methylglucoside are remarkable. The "rotation constant" k (which is numerically equal to the "absolute rotation," a_0, *i.e.* the rotation which would be observed at wave-length, $\lambda = \sqrt{1 + \lambda_0^2}$) is represented by two values which differ from the mean by only $\pm$ 0·01°, an error of 1 part in 2,000. The "dispersion-constant," which shows a difference of one unit in the third significant figure, is really (in spite of appearances) still more accurate. Three units in this decimal correspond with a difference of one unit in the third decimal of the dispersion-ratios ; the two values given for λ_0^2 correspond therefore with a difference from the mean of 1 part in 10,000 in the actual readings. There can therefore be no doubt whatever as to the validity of the simple dispersion formula to represent the experimental data for this complex substance.

The figures for the β-methylglucoside are less concordant, in part because the readings are 5 times smaller ; but they agree sufficiently well to show that there is no large deviation from the simple dispersion law.

It will be seen from the illustrations given above that the development of the enclosed cadmium arc promises to inaugurate a new era in the measurement of *simple rotary dispersion*. With the help of the new apparatus it will be possible to determine the two fundamental constants of any optically active compound by two methods of equal exactness. Further, the agreement of the two pairs of figures will serve as a check, not merely on the accuracy of the readings (in itself a very important advantage), but also on the strict validity of the dispersion formula in the case of each individual substance.

It is a pleasure, in conclusion, to acknowledge the valuable help that has been received in connection with this work from the Dixon Fund of the University of London.

GUY'S HOSPITAL,
LONDON, S.E.

RELATIONS BETWEEN THE ROTATORY POWERS OF THE MEMBERS OF HOMOLOGOUS SERIES.

Dr. Robert Howson Pickard and **Mr. Joseph Kenyon** read a Paper on "Relations between the Rotatory Powers of the Members of Homologous Series."

Attempts to discover a connection between the rotatory power and chemical constitution of a compound have been numerous since Crum Brown and Guye independently, in 1890, brought forward the theory connecting mass and molecular rotatory power. This now discarded theory has stimulated a large amount of research, the results of which up to 1904 have been summarized by Walden* and since then up to 1912 by Frankland.† The comparative failure (as regards the solution of the problem under consideration) of all this painstaking and laborious work led the present authors to plan a fresh investigation of the problem. Their results ‡ are as yet very incomplete, and have so far yielded no definite solution of the problem, but are put forward as a basis of discussion, as they appear to indicate some (at least) of the causes of the comparative failure of the earlier investigations.

Previous investigators have studied as a rule the effect of various substituents on the rotatory power of some *one* optically active compound—in the great majority of cases, the effect of substituting the alcoholic or carboxylic hydrogen atoms in tartaric, glyceric, and malic acids and in borneol and menthol. It is highly significant, in view of some of our later results, that, almost without exception, the homologous series mentioned in the two summaries quoted above are all composed of esters, a class of compounds which it would now appear are particularly prone to exhibit *anomalous* rotatory dispersion. To this, and to the once universal custom of determining the rotatory power for sodium light only, as well as to the very frequent disregard of the effects of temperature and even of solvents, a great deal of the present confusion in the interpretation of the older results is most probably due.

When planning a reinvestigation of this problem, the authors determined to synthesize and examine optically active compounds of the simplest possible chemical constitution, each containing only one asymmetric carbon atom and, as far as possible, having the various radicles (the effect of which on the rotatory power was to be studied) attached directly to it. At first it appeared desirable to restrict the investigation to the examination at different temperatures of homogeneous liquids, but it has since been found that some well-marked relations (due solely to the molecular configuration) which exist between the rotatory powers of the members of some series could only

* *Ber.*, 1905, **38**, 345.

† *J.C.S.*, 1912, **101**, 654.

‡ See *J.C.S.*, 1911, **99**, 45 ; 1912, **101**, 620 and 1427 ; 1913, **103**, 1083 ; 1914, **105**, 94 ; *Proc. C.S.*, 1912, **28**, 42 ; 1913, **29**, 296 ; *Ber.*, 1912, **45**, 1592.

be observed in solution, as they are masked at all temperatures up to the boiling-point when the compounds are examined in the homogeneous state.

So far there have been synthesized and systematically examined about forty secondary alcohols and some ninety esters derived from them. These are all of the general formulæ $R_1 \cdot CH(OH) \cdot R_2$ and $R_1 \cdot CH(O \cdot CO \cdot R_3) \cdot R_2$ respectively, where R_1, R_2, R_3 are normal alkyl radicles and comprise the following eleven homologous series of optically active compounds :—

(i) The carbinols of the series $CH_3 \cdot CH(OH) \cdot R$, hereafter called the "methyl" series.

(ii) The acetates of these carbinols, $CH_3 \cdot CH(O \cdot COCH_3) \cdot R$.

(iii) The dodecoates of the same, $CH_3 \cdot CH(O \cdot COC_{11}H_{23}) \cdot R$.

(iv) The esters of butan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_2H_5$.

(v) The esters of pentan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_3H_7$.

(vi) The esters of hexan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_4H_9$.

(vii) The esters of heptan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_5H_{11}$.

(viii) The esters of octan-β-ol, $CH_3 \cdot CH(O \cdot COR)C_6H_{13}$.

(ix) The esters of undecan-β-ol, $CH_3 \cdot CH(O \cdot COR)C_9H_{19}$.

(x) The carbinols of the series $C_2H_5 \cdot CH(OH) \cdot R$, hereafter called the "ethyl" series.

(xi) The carbinols of the series $(CH_3)_2CH \cdot CH(OH) \cdot R$, hereafter called the "*iso*propyl" series.

Each of the compounds comprising these series contains only one asymmetric carbon atom and is of the simplest possible chemical constitution, this latter being moreover similar for all the compounds.

The relation between the rotatory powers of the members of these series can be readily explained in a qualitative sense by a consideration of the size of (or space occupied by) the radicles attached to the asymmetric carbon atom. Thus, representing the compounds by the symbols C*abcd*, the effect of increasing the size of *d* (representing the "growing chain" in a series) is to alter in a more or less regular manner (usually to increase) the molecular rotatory power of the compounds. In the "methyl" series the space occupied by *a*, *b*, and *c* is the smallest conceivable (CH_3, H, OH) and the values of the molecular rotatory power when measured in the homogeneous state increase regularly by small increments as the chain grows. In solution (ethyl alcohol and benzene), however, the rotatory powers of individual members of the series are considerably exalted when the whole molecule itself approximates in configuration to a ring structure, as in pentan-β-ol and decan-β-ol, or when the growing chain in a similar manner all but returns on itself, as in methyl amyl carbinol (heptan-β-ol) and methyl decyl carbinol (dodecan-β-ol). When, however, the space occupied by the groups or atoms represented by *a*, *b*, and *c* is larger, the increase in molecular rotatory power, as *d* increases, becomes less regular. Either (1) it may be specially affected when the chain returns on itself, as in the "ethyl" series, where ethyl amyl, ethyl decyl, and probably ethyl pentadecyl carbinols (both in the homogeneous state and in solution) have values for the molecular rotatory power which are above those of the immediately preceding and succeeding members of the series, or (2) the increase may be relatively large until the growing chain *d* contains five carbon atoms with an increase of a much smaller order in the molecular rotatory power of successive members. This, for example, occurs in all the series of esters (except Nos. ii and iii) mentioned above, in which there is a rapid increase in the value of the molecular rotatory power $[M]_D^{20^\circ}$ for each member of the series up to the valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the stearate when these are examined in the homogeneous state at 20°. When, however, the space occu-

pied by the groups *a*, *b*, and *c* is still greater, the "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms. Thus in the series of dodecoates, where the group $—O·CO·C_{11}H_{23}$ is large, the molecular rotatory powers increase in value rapidly up to that for $C_4H_9·CH(O·COC_{11}H_{23})CH_3$ with a much smaller increment beyond. Results of a similar character have been observed in the "*iso*propyl" series of carbinols. When examined in the homogeneous state, the member containing four carbon atoms in the growing chain has the conspicuous value for the molecular rotatory power; on the other hand, in ethyl-alcoholic solution it is the member containing five carbon atoms in the growing chain which has the conspicuous value.

In the series of acetates particularly instructive results have been obtained. Here the grouping $—O·CO·CH_3$ is the smallest of the corresponding groups in the compounds examined, and it is found that the values of $[M]^{20°}$ decrease rapidly in the series until the member $C_6H_{13}·CH(O·CO·CH_3)·CH_3$ is reached, after which the rate of decrease becomes very much smaller. It should, however, be noted that in all the series of esters the growing chain —CO·R is attached only indirectly to the asymmetric carbon atom by means of another oxygen atom.

By including the examination of these esters in the investigation, the authors' original plan has been abandoned, but this is justified as the optical rotatory dispersions of the esters in general offer such a striking contrast to those of the carbinols. Thus for the latter it has been observed that (1) in an homologous series the rotatory dispersion ratio becomes constant (within the limits of experimental error) as soon as the growing chain has become distinctly the largest group attached to the asymmetric carbon atom and (2) the value of the ratio for a given carbinol is constant between wide temperature limits (20° to 200°), whereas for the esters (except perhaps for some of the β-butyl esters) these generalizations do not hold.

The rotatory powers of the esters as a rule are decreased (often to the extent of changing the optical sign) by solvents and by increase of temperature, the depressing effect for each set of conditions being a similar one for each of the different series. By suitable choice of conditions either of temperature or of concentration in some such solvents as carbon bisulphide, pyridine or benzene, the esters can be *caused* to exhibit anomalous rotatory dispersion. These conditions must be such that the $[\alpha]_D$ of the *d* ester is depressed so that it lies between $+2·5°$ and $\pm 0°$. It has been shown above how in a qualitative sense the relations between the molecular rotatory powers of the esters when measured at 20° in the homogeneous state can be explained, but such explanation would probably have been impossible had the temperature at which the comparisons were made been selected at above 150° when so many of the esters exhibit anomalous dispersion.

The results appear to be due to alterations in the complexity of the molecules and can be co-ordinated on the assumption that each ester is a mixture of two isomers, which have rotatory powers of opposite sign and different dispersive power. Such co-ordination is effectively brought out by the construction of "characteristic diagrams" drawn in the manner described by Armstrong and Walker.*

The present authors therefore suggest that (1) in general two forms of any one ester can exist; (2) the proportion of these two forms present varies according to the conditions of temperature or solution; (3) the difference is due to the exercise of the supplementary valency of the oxygen atom in one of the forms, and (4) when the two forms differ in dispersive power and

* *Proc. Roy. Soc.*, 1913, A, **88**, 388.

optical sign, anomalous dispersion may be observed. In an homologous series of esters the effect of the growing chain on the rotatory powers of the two isomers (supposed to be present) would be likely to vary in a more or less regular manner throughout the series. In the series of esters mentioned above, since the region in which anomalous dispersion has been observed lies near to $\pm 0°$ the dispersive powers of the isomers cannot be very widely different in the case of any of the compounds, whilst if there be any connection at all between chemical constitution and rotatory power the values of the rotatory power of the various esters should bear some relationship, as all the radicles are alike. No numerical relation has so far been observed—it is not yet possible to choose a set of conditions suitable for instituting comparisons —but it is significant that the *same* characteristic diagram appears to correlate all the determinations of the rotatory power of one of the optical antipodes of the compounds comprising the eleven series mentioned above, in addition to other derivatives of the carbinols themselves.

In this respect the properties of *l* methyl *α* naphthyl carbinol are very instructive. It melts at 47°, but will remain in the supercooled state and at 10° it has $[\alpha]_{\underset{\text{violet}}{Hg}} - 8{\cdot}0°$, showing at and within a few degrees of this temperature anomalous dispersion; at 120° it has $[\alpha]_{\underset{\text{violet}}{Hg}} - 77{\cdot}4°$, at and above which temperature the dispersion remains approximately constant. In 5 per cent. carbon bisulphide solution it has $[\alpha]_{\underset{\text{violet}}{Hg}} - 198{\cdot}9°$, whilst it forms a dextro-rotatory hydrogen phthalic ester, which in 5 per cent. ethyl alcoholic solution has $[\alpha]_{\underset{\text{violet}}{Hg}} + 171{\cdot}7°$. These determinations range over 370° and can be correlated on *one* characteristic diagram. It can be assumed here that (1) two forms of the carbinol with different dispersive power and of opposite optical sign exist, owing to different dispositions of the valencies in the naphthyl radicle; and (2) the rotatory powers of these two forms and their esters are *principally* determined by the groups attached to the asymmetric carbon atom.

At least it seems now capable of proof that the rotatory power of a derivative of a given optically active compound *is* some function of the rotatory power of the latter, although the highly constitutive character of this physical property makes the problem still one of extreme complexity.

THE DEPENDENCE OF ROTATION ON TEMPERATURE, DILUTION, NATURE OF SOLVENT, AND WAVE-LENGTH OF LIGHT.

Dr. T. S. Patterson read a Paper on "The Dependence of Rotation on Temperature, Dilution, Nature of Solvent, and Wave-length of Light."

Some twenty years ago the general opinion in regard to the influence of temperature on the rotation of an optically active substance probably was that the rotation, as in the case of a substance like ethyl tartrate, tended towards a constant value at higher temperatures, that the temperature-rotation curve became asymptotic to the axis of temperature. In 1896, however, it was shown by Frankland and Wharton in the case of ethyl dibenzoyl tartrate* that a minimum rotation could exist, and some years later Winther,† in an investigation connected with rotation-dispersion, fitted a parabolic expression to a number of temperature-rotation curves and made the assumption that since the parabola has a maximum therefore the rotation of these substances should also pass through a maximum value. Somewhat later still the present writer showed ‡ that this maximum actually exists, although at a different temperature from that deduced by Winther, and showed also that the maximum, instead of occurring at a constant temperature in a series of homologous compounds, or on dilution of an active substance with an indifferent solvent, moves gradually through a range of temperature. Thus in nitrobenzene, for instance, the maximum rotation of ethyl tartrate, which occurs at a temperature of about 175°, moves rapidly towards a lower value as the solution becomes more dilute, the rotation, at the same time, becoming gradually greater. It thus becomes immediately clear why the rotation of a dilute solution of ethyl tartrate in nitrobenzene diminishes with rise of temperature whilst the rotation of the ester itself and of its more concentrated solutions in nitrobenzene increases on heating; in the former case the ordinary temperature is on one side of the maximum, whilst in the latter case it is on the other. The temperature coefficients of all solutions of ethyl tartrate in nitrobenzene are less than that for the pure ester; nitrobenzene at the ordinary temperature has a powerful elevating effect on the rotation of this particular active compound. A number of other substances, however, of which acetylene tetrabromide may be taken as the best example, have an opposite effect. These substances have a considerable power to depress the rotation of the ester, and in agreement with this it is found that the temperature coefficient of all solutions made up of ethyl tartrate and that

* *Trans. Chem. Soc.*, 1896, **69**, 1587.
† *Zeitsch. Phys. Chem.*, 1902, **41**, 176.
‡ *Trans. Chem. Soc.*, 1908, **93**, 1843.

solvent have temperature coefficients which are greater than that of the pure ester. It may therefore be inferred that in these cases the maximum rotation would persist but would move towards a still higher temperature, which in this particular case has not yet been actually observed.*

Further, it has been found that other solvents produce effects of a closely similar kind in such a way that if, for instance, a solution in water and one in nitrobenzene have one and the same rotation at some given temperature, then the temperature-rotation curves of the two solutions will be closely similar, although the concentrations may be entirely different. Thus the curve for a number of different solvents at various concentrations blend into a diagram remarkably like that for one single solvent at a number of concentrations, and it would seem as if we might almost eliminate from consideration the nature of the inactive solvent and the concentration since the course of the temperature-rotation curve is apparently defined by the rotation at any given temperature.† When the influence of a particular solvent appears to be exhausted—that is, when its maximum influence has been reached in a dilute solution—the influence may be taken up, as it were, and carried on by another one more powerful. Thus α-nitronaphthalene, $p = 25$, has approximately the same effect as nitrobenzene, $p = 5$, so that the α-nitronaphthalene at $p = 25$ appears to pick up the influence of the nitrobenzene at that point and carry it farther.

Another matter of interest in connection with the relation between temperature and rotation is the following. It has been found that certain substances, such as ethyl tartrate, show a maximum rotation, whereas some derivatives of that compound, for instance ethyl ditrichloroacetyltartrate, show on the contrary a temperature of minimum rotation, and a reconciliation of this exactly opposite behaviour must obviously present some difficulty. Possibly, however, the reconciliation may be effected in this way. It is known that the substitution of an alkyl radicle, such as *n*-propyl, *iso*-butyl, etc., for ethyl, in ethyl tartrate, moves the maximum rotation towards a lower temperature whilst at the same time the actual value of the rotation is increased,‡ and it seems reasonable to suppose that the very much greater change involved in the replacement of the hydroxylic hydrogen by the trichloroacetyl group should produce a correspondingly greater shifting of the temperature of maximum rotation. The maximum may, in fact, be shifted out of the region of ordinary temperatures altogether and the portion of the curve for the ditrichloroacetyl derivative may correspond with some part of the graph for ethyl tartrate, a part with which we are unacquainted, only because we are not able at present to investigate the problem over a sufficient range of temperature. An examination of some of the data which have been obtained by various observers in the investigation of certain active substances over a fairly wide range of temperature strongly supports this view, for it is found that not only do maxima and minima exist in different curves, but that in the same curve not infrequently a maximum or a minimum together with a point of inflection may be observable.

No investigation has yet been carried out over a sufficient range of temperature to reveal both a maximum and a minimum.§

The temperature-rotation curve of an active compound is thus probably

* Such evidence as exists in regard to this question will be found in a paper in the *Transactions of the Chemical Society* for 1913, **103**, 145, especially, perhaps, p. 171.

† See Fig. 3, *Trans. Chem. Soc.*, 1908, **93**, 1846.

‡ *Trans. Chem. Soc.*, 1913, **103**, 148.

§ This question has been fairly fully discussed elsewhere (*Trans. Chem. Soc.* 1913, **103**, 151).

periodic, that is, may show several maxima and minima, and it seems probable that the influence of a solvent is simply to shift the complete curve of the homogeneous substance in one direction or another, but, of course, probably with minor alterations. Thus for ethyl tartrate the influence of nitrobenzene seems to be to shift the whole curve simultaneously towards a lower temperature and a higher rotation.

Rotation Dispersion.—Another very interesting question relates to the position of the maximum rotation for different colours of light. This is a subject which has been thoroughly investigated in only very few cases, but it would appear from the results which have been obtained that the maximum does not necessarily occur at the same temperature for different colours of light. Only two substances have been examined, ethyl tartrate and *n*-propyl tartrate, and in both the maximum rotation moves towards a higher temperature as the wave-length of the light becomes less.* The temperature-rotation curve for violet light is thus apparently retarded on the temperature-rotation curve for yellow or for red light.

This is chiefly important in connection with what is called rotation dispersion. It is well known, of course, that the rotation of an active substance usually depends on the wave-length of the light used, and it is often stated that the rotation for violet light is greater than that for red. If, on the diagram showing the temperature-rotation curves for different colours of light in the case of ethyl tartrate, a vertical line be drawn through the temperature 160° it will cut the temperature-rotation curves† in the order violet, blue, green, yellow, red, and if these values be plotted on a new diagram relative to wave-length a graph will be obtained which is always, so far as the writer is aware, a curved line. If the line be drawn, however, at a temperature of say, 80°, it would cut the temperature-rotation curves in the order, blue, green, violet, yellow, red, and on plotting these values of rotation against wave-length a dispersion graph would be obtained rising from red to a maximum at blue and descending again to violet. Such a curve is generally said, without any proper reason, to be abnormal. At some wave-length intermediate between the extremes there is a rotation maximum. If now a line be drawn through the temperature —40° the sequence of the rotation values will be the same as at first, but the violet light gives the lowest rotation, a negative rotation being regarded as less than a positive rotation. This is, however, a purely accidental circumstance and is solely due to the fact that the temperature-rotation curves for ethyl tartrate happen to pass through the point of inactivity in the neighbourhood we are considering, otherwise the values for violet would be numerically less than for red. It is quite essential that in discussing rotation-dispersion some method must be devised which shall eliminate the sign of the rotation, and it would seem desirable to designate the dispersion on one side of the region of intersection of these curves as positive and that on the other as negative.

The rotation-dispersion is often defined as the ratio of the rotations for various colours of light to the rotation for one given colour of light such as red or yellow, but it has been carefully pointed out by Winther‡ that this is a very unsatisfactory procedure giving most misleading values for rotation-dispersion as in the case of methyl tartrate. This point has been overlooked quite recently by Armstrong and Walker and by Pope and Winmill. The latter authors have measured the rotation, for three different lines of the spectrum, of derivatives of tetrahydroquinaldine, and in regard to the *o*-nitrobenzoyl

* *Trans. Chem. Soc.*, 1913, **103**, 165, 166.
† *Trans. Chem. Soc.*, 1913, **103**, p. 165, Fig. 7.
‡ *Zeitschr. Phys. Chem.*, 1902, **41**, 205.

derivative state* that this substance exhibits quite abnormal rotation constants, whilst with regard to the 2-nitrotoluene-4-sulphonyl derivative† they say, "The considerable variation of rotatory dispersion of the latter substance with the solvent used is noteworthy."

Armstrong and Walker comment on what they term the abnormal dispersive power of these substances and remark,‡ "It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned." The rotatory dispersive power of these substances is, however, not more abnormal than is that of any of the other compounds examined by Pope and Winmill. The explanation, in the first case at least, is in fact merely arithmetical, the cause of any anomaly that exists being identical with that discussed by Winther in the case of methyl tartrate already referred to, namely, that in certain of the solvents used, the rotation of the active compound passes through the point of inactivity, and that by applying an arithmetical process by a purely rule of thumb method to numbers sometimes negative and sometimes positive, one is bound to obtain quotients also sometimes positive and sometimes negative, but this only indicates that the abnormality ought not to be laid at the door of the substance examined.

The second of these two cases is, however, of considerable interest and will be referred to farther on because it raises an interesting question in connection with normal rotation-dispersion, but before dealing with it we may revert for a moment to the case of ethyl tartrate in regard to abnormal rotation-dispersion. We have seen that at a temperature of about 80° the dispersion-rotation curve shows a maximum in the neighbourhood of the blue light, but that if the temperature be 160° there is no such maximum for these particular colours and that the same is the case if the temperature be about —40°. To say, however, as is often done, that the rotation-dispersion at the high and low temperatures is normal whereas at the intermediate temperature it is abnormal seems very arbitrary. It must be clear that if the other two curves were extrapolated so as to include in the former case light of wave-length considerably less than violet, a maximum would be very likely to appear in the curve, whilst at the lower temperature of —40°, if the rotation-dispersion curve were extrapolated, a maximum would occur, with equal probability, for light of greater wave-length than red. The term abnormal, if it is to be used at all, should be applied, not merely to the temperature-rotation curve at one temperature, but to the temperature-rotation curves for all temperatures, in fact, to the substance itself. The reason for abnormal rotation-dispersion in the light of what has already been said as regards the maximum in temperature-rotation curves seems simple. The whole curve for violet light is retarded on that for blue, that for blue is retarded on that for green and so on, the result being that the maximum passes to a higher temperature as the wave-length of the light decreases. In the same way, since the whole curve is displaced, and since, as appears to be the case, the sweep of these curves is the same also, they intersect one another at different points, not all at one point, and this gives rise to the phenomenon of anomalous rotation-dispersion.

It may be remarked in this connection that attention has often been drawn to the fact that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this seems clear from what has just been said. It is at a distance from a maximum—roughly speaking, midway between a maximum and a minimum—that rotation changes most rapidly with alteration of temperature, and it is just in this

* *Trans. Chem. Soc.*, 1912, **101**, 2311.
† *Loc. cit.*, 2316.
‡ *Proc. Roy. Soc.*, 1913, A, **88**, 391.

region that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

The question now arises, what is normal rotation-dispersion? or, to put it otherwise, do any substances exist which differ in their behaviour from ethyl tartrate? This is a question which cannot be settled at the present time, since, although a considerable amount of material has been collected, it scarcely touches the main question because the all-important matter of temperature-change has been left out of account. Nevertheless, very many statements may be found in the literature to the effect that this substance or that has normal rotation-dispersion, and the idea seems generally to be that if the dispersion coefficient varies comparatively little, perhaps when the compound is mixed with a solvent or when its temperature is altered slightly, then the rotation-dispersion is to be considered as normal. An example in which the temperature-change was very considerable is afforded by the dispersion data obtained by Pickard and Kenyon.* But it is, nevertheless, difficult to decide whether these substances really have normal rotation-dispersion or not. The matter may be considered in this way. It will probably be granted that the rotation of a substance for any colour of light varies at least to some extent as the temperature changes, as is the case, for instance, with the rotation of the alcohols prepared by Pickard and Kenyon. Now let us imagine that the rotation for a given substance for violet light at a temperature t is A, and for red light is B, then the dispersion coefficient is $\frac{A}{B}$†; now suppose the temperature to change to t' and the rotation for violet light at this temperature to be A′, and suppose that this is less than A, that is, that the rotation diminishes as the temperature falls, let us say, from t to t', then in order that the dispersion coefficient may be the same as before we must have $\frac{A'}{B'} = \frac{A}{B'}$ B′ being the rotation for the red light at the temperature t'. Now it will be obvious that this ratio can only be preserved provided the two temperature-rotation curves for violet light and for red light are such that they intersect at the point at which the rotation for both colours of light is zero, and that beyond the temperature at which this occurs they proceed again in a similar manner, but with negative, instead of positive, rotations. From such examples as we know it is impossible to decide whether this behaviour will be, in any way, general—whether temperature-rotation curves will cut in a single point just where the rotation is zero—and it seems to the writer that the apparent normality of certain rotation-dispersions is to be ascribed to the fact that these dispersion coefficients have been measured on substances the temperature-rotation curves of which happen to have a maximum value in the neighbourhood of ordinary temperatures,‡ and are not due, or at least not necessarily due, to any inherent peculiarity of the substances themselves. But, of course, Pickard and Kenyon's alcohols may represent a class of substances conforming exactly to the type for which the temperature-rotation curves meet exactly at zero rotation.

Nevertheless, it may, after all, be essential to distinguish between two different classes of compounds. We have seen already that the family of temperature-rotation curves for a substance such as ethyl tartrate do not all cut in one point, and this, we have seen, was due to the fact that the maxi-

* *Trans. Chem. Soc.*, 1913, **103**, 1933.

† This is the ordinary way of looking at the matter. Winther's method is much better, but for reasons which cannot be entered on here it also would probably fail if applied over a wide range of temperature.

‡ As is the case with Pickard and Kenyon's alcohols.

mum rotations for the different colours lie at different temperatures. Now it is quite possible that in certain other cases the maximum rotation for different colours of light may perhaps lie at the same temperature, in which case, if the sweep of the different curves were the same, the whole family of curves would cut in a single point, but of course it does not follow in any way that the rotation corresponding with the points in which they cut should be zero. No such instance as this has quite definitely been observed, but perhaps the data obtained by Pickard and Kenyon for optically active alcohols may represent a case of this sort, which would account for the comparative constancy over a wide range of temperature of the dispersion coefficients, which happen to lie more or less in the neighbourhood of the maximum rotation. It is even more probable that the data already referred to, obtained by Pope and Winmill for 2-nitrotoluene-4-sulphonyl *l*-tetrahydroquinaldine, may be of the same sort. From a study of their data for this substance, it seems very likely that, if a solvent could be found in which the active compound would have a rotation of about $-85°$, the rotation would be identical at least for the three colours of light which they used, and perhaps it might be identical even for a wider range of colours than this.

These two classes of substances may be illustrated by two of the diagrams in the paper by Armstrong and Walker * already referred to. In that paper these authors have arrived at the conclusion that change of rotation, both with alteration of temperature and of solvent, is to be ascribed to a variation in the relative proportions of dynamic isomerides. Limitations of space render it impossible to point out the enormous objections which could immediately be brought against any such idea. It need only be remarked here that Armstrong and Walker's diagram on p. 398 is only another method of representing rotation-dispersion, in which the values of the rotation are plotted relative to the rotation instead of relative to wave-length, and that they do not necessarily have anything whatever to do with the presence or absence of dynamic isomerides. Since this diagram therefore merely represents dispersion data in a new way, the deductions which can be made from it are exactly those which could be made from ordinary dispersion-rotation curves, but inasmuch as the diagram depends upon a purely arbitrary assumption, it is of course of less value. It is to be noted that the lines for the different colours drawn on their diagram intersect practically at a single point, and that the diagram differs from those on p. 397 for methyl and ethyl tartrate exactly in this respect.

These two diagrams of Armstrong and Walker represent the same thing as is shown in the diagram Fig. 7 of a paper by the present writer † for ethyl tartrate, where there is also an intersection of temperature-rotation graphs throughout a certain range. It may possibly be that substances really exist in two classes, those for which the temperature-rotation curves or Armstrong and Walker's dispersion curves cut in a single point and those for which they cut over a range of temperature or rotation, but this is likely to be the only difference which can be discovered in regard to rotation-dispersion between various active compounds. Whether it will be wise to label one as normal and the other as abnormal remains to be seen.

Only one further matter need be referred to, namely, rotation-dispersion in solution. It has been shown by the present writer that the temperature of maximum rotation of a substance such as ethyl tartrate moves to a different temperature as the concentration is varied. Very few substances have been examined for different colours of light in various solvents and at several

* *Proc. Roy. Soc.*, 1913, A, **88**, 388.
† *Trans. Chem. Soc.*, 1913, **103**, 165.

concentrations, but it appears very clearly from the data which have been collected by Winther for tartaric acid in water and in alcohol, that the period of intersection of the temperature-rotation curves is very similar in solution to what it is for the homogeneous substance, and further, that on dissolving the compound in a liquid this period of intersection shifts its position on a diagram in exactly the same kind of way that the maximum rotation shifts its position.* It seems, therefore, extremely probable, in fact it seems certain, that the so-called normality of the rotation-dispersion of, say, tartaric acid in water is solely to be ascribed to the fact that the influence of the solvent is to move the maximum of the temperature-rotation curves into the ordinary temperature, and at the maximum rotation the so-called dispersion coefficient appears to be normal. This greater normality is, however, altogether imaginary, since the abnormality has merely been shifted to a different region of temperature. It is for a similar reason that the rotation-dispersion of the alkali tartrates appears to be normal.

It may perhaps be mentioned in conclusion that by the adoption of the point of view advocated in this paper and in *Trans. Chem. Soc.*, 1913, **103**, 145, a survey of all the phenomena of optical activity may be made and a comprehension of the interdependence and interrelationship of these phenomena be obtained, and in addition it may be observed that this advantage is gained independently of any theory as to the ultimate causes of the phenomena discussed. The writer's own working hypothesis as to the mechanism of these changes has been detailed in various papers, and it is perhaps only necessary to say here that the statement by Pope and Winmill,† which is prominently quoted by Armstrong and Walker,‡ to the effect "that he has abandoned the view that internal pressure is an operative factor in connection with variations in the rotatory power," is incorrect.

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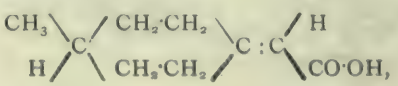
March 16, 1914.

* See *Trans. Chem. Soc.*, 1913, **103**, 167, Fig. 9.
† *Trans. Chem. Soc.*, 1912, **101**, 2313.
‡ *Proc. Roy. Soc.*, 1913, A, **88**, 390.

THE RELATION BETWEEN OPTICAL ACTIVITY AND MOLECULAR COMPLEXITY.

A Paper on "The Relation between Optical Activity and Molecular Complexity" was contributed to the Discussion by **Professor William Jackson Pope, F.R.S.**, and **Mr. John Read.**

For many years after the enunciation of the doctrine of the asymmetric carbon atom by van't Hoff and LeBel in 1874 no instance was known of an optically active substance which did not contain an asymmetric carbon atom; such substances do not occur in nature, and, when they were prepared in the laboratory, the experimental methods available proved insufficient to effect the resolution of the externally compensated synthetic products. The first optically active substances containing no asymmetric carbon atom to be described were the *d*- and *l*-benzylphenylallylmethylammonium iodides, $N(C_7H_7)(C_6H_5)(C_3H_5)(CH_3)I$ *; the isolation of these compounds, the optical activity of which is associated with the presence in the molecule of an asymmetric quinquevalent nitrogen atom, was quickly followed by the preparation of optically active substances containing, as an element of constitution, an asymmetric quadrivalent sulphur, selenium, or tin atom. Later it was shown that optically active substances can exist which, although necessarily possessing enantiomorphous molecular configurations, contain no atom which is asymmetric in the sense of the original definition; the *d*- and *l*-methylcyclohexylideneacetic acids—



of Perkin, Pope, and Wallach † were the first compounds of this type to be prepared. It is probably convenient to regard the optically active complex cobalt, chromium, rhodium and iron compounds recently obtained by Werner as possessing enantiomorphous molecular configurations not associated with asymmetry of any particular component atom.

The first fundamental demonstration by van't Hoff and LeBel that optical activity could be associated with asymmetry of one or more carbon atoms present in a particular molecule, proved that the constitutional formulæ assigned to certain organic compounds must be regarded as extended in three-dimensional space; a perusal of the contemporary literature indicates, however, that this extension of view was of a localized character—that it only embraced the particular class of optically active compounds then known—and that it was not immediately seen that stereochemical formulæ are of general applicability. The developments briefly summarized above,

* Pope and Peachey, *Trans. Chem. Soc.*, 1899, **75**, 1127.
† *Trans. Chem. Soc.*, 1909, **95**, 1789.

together with the work done on *cis*- and *trans*-isomerism and mutarotation, have made it quite clear that all constitutional formulæ, both of organic and inorganic substances, only provide a satisfactory means of representing, statically and dynamically, intermolecular conditions and intramolecular change, when considered as built up in three-dimensional space.

The subject has, however, another aspect. The developments referred to above have resulted from the study of substances of complex constitution; it has indeed been customary for the purpose of extending stereochemical conclusions to study compounds possessing the maximum degree of molecular complexity compatible with certainty as to their molecular constitution. To a large extent experimental work has been largely influenced by the impression that a certain degree of molecular complexity is requisite before a substance of enantiomorphous molecular configuration can exhibit optical activity; the prevalence of this feeling finds support in the facts that no optically active substance has been hitherto described which contains fewer than three carbon atoms in the molecule and that no resolution of the salts of mixed tertiary amines has yet been effected.

In view of the work now to be described, it appears, however, that optical activity is exhibited by substances of enantiomorphous molecular configuration even of the most simple molecular composition; the idea must thus be abandoned that the exhibition of stable optical activity is only possible when the substance concerned possesses considerable molecular complexity.

On crystallizing chloroiodomethanesulphonic acid, $CHClI{\cdot}SO_3H$, with a number of optically active alkaloids no evidence of the resolution of the acid could be obtained, owing apparently to the formation of partially racemic salts. Careful fractionation of the salt of the acid with *d*- or *l*-hydroxyhydrindamine showed, however, that resolution into fractions of different rotatory power was effected; from the various fractions samples of ammonium *d*- and *l*-chloroiodomethanesulphonate of low dextro- and lævo-rotations were separated. The difficulty of effecting a complete resolution of the acid by means of hydroxyhydrindamine was so great that another method was sought; the following process, although tedious, was found to work satisfactorily.

On adding a solution of a brucine salt to one of ammonium *dl*-chloroiodomethanesulphonate, the alkaloid is precipitated almost quantitatively, the brucine salt being very sparingly soluble in water; the ammonium salt recovered from the precipitated brucine salt, prepared in the ordinary manner just indicated, is optically inactive. On adding to the solution of the ammonium salt one-fifth only of the amount of brucine sulphate solution requisite for complete precipitation, and separating the chloroiodomethanesulphonic acid and its ammonium salt from the deposited brucine salt, a product showing $[M]_{5461} + 19{\cdot}2°$ was obtained. The addition successively to the mother liquids of a second, third, fourth and fifth part of the requisite brucine sulphate led to the precipitation of salts which, on decomposition with ammonia, gave ammonium chloroiodomethanesulphonate of varying rotatory power, the fraction separated from the last part exhibiting $[M]_{5461} - 7{\cdot}4°$. These results indicate that the first fractional precipitation with brucine leads to a partial resolution of the acid, and the various samples of ammonium salt of different rotatory powers were therefore further fractionally precipitated with brucine sulphate in the same manner as at first. By frequent repetitions of this kind of process ammonium *d*-chloroiodomethanesulphonate of high rotatory power was slowly accumulated, and finally an ammonium salt exhibiting $[M]_{5461} + 43{\cdot}7°$ in dilute aqueous solution was obtained. This substance represents ammonium *d*-chloroiodomethane-

sulphonate in a state of considerable purity and its chemical identity was established by the ordinary methods.

This optically active substance of very simple molecular composition contains less than 5 per cent. of carbon, and it is noteworthy that the optical activity is very persistent. It is not appreciably affected by evaporation to dryness with ammonia or hydrochloric acid, by boiling with dilute caustic soda solution or by heating in a sealed tube with water for two hours at 130 — 150°.

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THE GENERAL INFLUENCE OF RESIDUAL AFFINITY UPON ROTATORY POWER, AND ITS PROPOSED APPLICATIONS.

Dr. Thomas Percy Hilditch contributed to the Discussion a Paper on "The General Influence of Residual Affinity upon Rotatory Power, and its Proposed Applications."

Optical rotatory power is admittedly a property most sensitive to the effects of chemical constitution, and this fact, on the one hand, should render it especially valuable as a physical asset in constitution determination; whilst naturally, on the other hand, it has made the problem of analysing the resultant effect (represented by the rotatory power of a compound) into its component parts (represented mainly by the constitutive "influences" mentioned) exceedingly difficult. It is obvious, indeed, that the solution of the question, in spite of the many investigations made during the past decades, is still far from complete, and it is permissible to inquire how far our present knowledge can safely be applied to the use of rotatory power in deciding the constitution of an organic compound.

It may be said at once that, in the writer's opinion, the presence of strongly unsaturated groups (particularly contiguous unsaturation and symmetrical conjugation) in certain positions in an optically active compound is accompanied by abnormal rotatory power. We have then to consider whether it is possible to obtain the numerical data indicating the "normal" rotatory power (as distinct from any irregular effects) as a basis for comparison and must therefore discuss the following points:

(*a*) The measurement of optical activity.

(*b*) Restrictions imposed by the complexity of the asymmetric system and the physical state of the compound.

(*c*) The nature of the rotatory power of corresponding and nearly related saturated compounds, *i.e.*, the choice of some kind of "series constant."

(*a*) *Measurement of Optical Activity.*

(i) *Variation of the Rotation with the Wave-length of Light.*—This question, which is receiving so much attention at the present time, has obviously an important bearing on the application of the bulk of existing data, which is based only upon the rotatory powers afforded by the sodium lines. It would seem from various statements made by chemists to whom we owe the rapidly accumulating data on rotation dispersion that considerable doubt must attach to the interpretation of any of the older figures, which of course represent only one point on the graph of rotations plotted against wave-length. But can it be thus assumed, with our present knowledge, that the old "D-line" figures are likely to be so erratic? Whilst appreciating the great advance made by the new system of measurement (and therefore entering with some diffidence upon even a partial criticism of the views of those who are developing this line of work) one would point out that a consideration of the rotation dispersion curves at present available for connected series of com-

pounds does not show that "anomalous" rotatory dispersion is the rule rather than the exception, and that consequently conclusions based on the values for a single ray of light cannot finally be discredited on this ground alone, except by re-examining the whole of the compounds in question in order definitely to determine in which cases the values for the D-lines fall on an irregular portion of the rotation-wave-length curve.

(ii) *Specific and Molecular Rotation.*—Tschugaeff * pointed out that specific rotatory power has little meaning either from the standpoint of the molecular hypothesis or of stereochemistry, whereas molecular rotatory power gives a direct comparison of the rotation produced by the active molecules. The further observation of Tschugaeff that molecular rotatory power in homologous series reaches approximate constancy after the earlier members (which the writer † has shown to be quite general except when disturbing influences such as those of unsaturation are present) is strong presumptive evidence of the importance of comparing molecular rather than specific rotations. Granting that comparison by molecular rotatory power is valid in these cases, why not in others? Professor Rupe ‡ feels that in comparing molecules of largely differing size (*e.g.*, $R \cdot CH_3$ and $R \cdot C_6H_5$) the use of molecular rotations attributes too great an influence to the bulk of the larger group; but is it not equally correct to say (on the assumption that molecular rotations are the more comparable) that the value obtained for the specific rotation in the latter case is too small, because the larger molecular weight thus has the effect of unduly increasing the divisor in the calculation—

$$\frac{100\,M}{\text{Mol. Wt.}} = a\,?$$

(*b*) *Restrictions imposed by Asymmetric Complexity and Physical State.*

In regard to the second of these it will be agreed that it is necessary to eliminate as far as possible chance irregularities due to association, solvent effect, etc., by the examination of substances both in the liquid state where possible and in a variety of solvents.

With reference to the question of asymmetric complexity, the writer is in hearty agreement with Professor Rupe's opening statement in his contribution to the General Discussion; it may be added that there is, after all, but little proof that the optical activity of a polyasymmetric grouping is derived in any way additively from the activity of each asymmetric atom. In the author's opinion § the balance of existing evidence is in favour of Pasteur's original proposition || that optical activity is due to *molecular* rather than to *atomic* asymmetry (the recent work of Perkin, Pope and Wallach ¶ and of Mills and Miss Bain ** yields important evidence for this view).

At all events, the following series of compounds following the Tschugaeff rule quoted above (with a variation of $[M]_D$ of less than 3 per cent.) is instructive:

3 series of compounds containing 1 asymmetric atom.
5 series of compounds containing 3 asymmetric atoms.
1 series of compounds containing 4 asymmetric atoms.
1 series of compounds containing probably 5 or 6 asymmetric atoms.

* *Ber.*, 1898, **31**, 360.
† *Trans. Chem. Soc.*, 1912, **101**, 195.
‡ *Supra*, p. 6.
§ Cf. *Trans. Chem. Soc.*, *loc. cit.*, p. 197.
|| *Compt. rend.*, 1852, **35**, 180.
¶ *Trans. Chem. Soc.*, 1909, **95**, 1755.
** *Ibid.*, 1910, **97**, 1866.

(It may also be remarked here that derivatives of malic and tartaric acids, chosen by many investigators presumably on account of their asymmetric simplicity, are unfortunately shown to be quite unsuitable for comparative work by the general results of the study of the marked influences of groups possessing residual affinity, since these substances contain hydroxyl and carboxyl groups directly attached to the asymmetric atoms. The irregular results so frequently obtained are doubtless largely due to this fact.)

(*c*) *The Choice of Some Kind of "Series Constant."*

Anomalies in rotatory power due to unsaturation must obviously be compared with the corresponding saturated compounds, and a few instances of such comparisons follow; it is now pretty generally recognized, by the way, that an "anomaly" need not necessarily mean a +ve increase of rotation, deviation in either sense from the normal order of rotation alone being implied.

In certain cases, such as esters in which the disturbing influence is in the acidic part of the molecule whilst the alcohol is the source of optical activity, or vice versa, the Tschugaeff rule may be used to give an approximate "series constant"; the constancy, it is true, may only hold to within 5 per cent., but since the anomalies noted are frequently of the range of 30 per cent. or over, this does not invalidate the comparison. If a derivative containing two or more of the optically active residues is under consideration, comparison must naturally be made between the "optically equivalent" rather than the molecular rotatory powers.

A few examples of menthyl esters and brucine salts of acids of varying constitution (but all practically completely saturated) will serve both to indicate the validity of Tschugaeff's law and to illustrate the preceding statements:

Acid.	Menthyl Ester.			Brucine Salt.		
	$[\alpha]_D$	$[M]_D$	$[M]_D$/No. of opt. active groups.	$[\alpha]_D$	$[M]_D$	$[M]_D$/No. of opt. active groups.
n-Butyric* ...	−71·33	−161·2	−161·2	−51·33	−247·4	−247·4
Palmitic* ...	39·79	156·8	156·8	38·07	247·5	247·5
Glutaric† ...	80·26	328·3	164·2	50·62	465·8	232·9
Sebacic† ...	67·08	320·6	160·3	48·24	477·5	238·8
Carbonic‡ ...	92·52	312·7	156·4			
Orthosilicic §	95·24	617·1	154·3			

In the next place, if optical activity is to be of any extended service, derivatives of (rather than simple optically active) compounds *must* perforce be used, for it will only be in rare cases that the compound which it is desired to study will of itself be optically active. Since derivatives are only produced by means of reactions taking place at groups possessing residual affinity, such a group must remain interposed between the studied centres of residual affinity and the optically active nucleus. This interposed residue has considerable effect upon the nature of the anomaly caused by the studied unsaturation. The phenomenon appears to be very roughly similar to that of the superposition of colours: thus, whilst the eye (corresponding to the asymmetric part of the molecule) can readily differentiate varying shades

* *Trans. Chem. Soc.*, 1912, **101**, 199.
† *Ibid.*, 1909, **95**, 1581.
‡ *Ibid.*, 1908, **93**, 1388.
§ Tschugaeff, *Journ. Russ. Phys. Chem. Soc.*, 1902, **34**, 696

of yellow light (corresponding to the unsaturation under investigation), if a blue medium (representing the carboxyl residue in the case of an ester) be interposed, not only is it more difficult to distinguish between the various shades of yellow, but all appear as various tints of green.

The case of Pickard and Kenyon's excellent series of alcohols is instructive, for here, where no such uniting group is present, the Tschugaeff rule is not followed quite so closely as in compounds of the ester or salt type in which residual affinity is present between the "growing chain" and the "asymmetric carbon atom," but on the other hand the presence of a phenyl or naphthyl group creates proportionately greater disturbance than is the general rule in compounds of the latter type.

The Effect of Conjugated Unsaturation.

This subject has been treated very fully in Professor Rupe's contemporary paper, and the writer can add but little to his comprehensive proof of the marked effects of such systems on rotatory power; it may be well to point out that the Professor has apparently misunderstood the author's previous statements on the relative influences of conjugation and of spacial proximity of the unsaturation to the optically active nucleus, which were to the effect that *both causes do undoubtedly contribute*, although conjugation is in general the predominant factor. It may be recalled that the writer * has, indeed, encountered certain instances of enhanced optical activity due solely, as far as could be judged, to the spacial proximity of unsaturated groups which were not even chemically united.

"Symmetrical Conjugation." †

One of the most striking effects of conjugation is observed when the entire optically active molecule is symmetrical about the centre of the conjugated system. As this principle has been used in one of the applications of optical activity to constitution determination cited below, a few typical examples may be quoted here:

	$[M]_D$	Difference.
Camphor,‡ $C_{10}H_{16}O$	+ 67·2	—
Camphor-β-mercaptan, $C_{10}H_{15}O \cdot SH$	+ 11·0	− 56·2
Dicamphoryl-β-disulphide, $C_{10}H_{15}O \cdot S \cdot S \cdot C_{10}H_{15}O$...	− 355·2	− 244·8
Aminocamphor,§ $C_{10}H_{15}O \cdot NH$	+ 35	—
Iminocamphor, $C_{10}H_{15}O : NH$	+ 151	+ 116
Azocamphanone, $C_{10}H_{15}O \cdot N : N \cdot C_{10}H_{15}O$	+ 790	+ 360
Diethyl tartrate ‖	+ 18·9	—
Diethyl monoacetyltartrate (no conjugation with —COO—)	+ 23·1	+ 4·2
Diethyl diacetyltartrate (symmetrical, but no conjugation)	+ 9·9	− 9·0
Diethyl monobenzoyltartrate (conjugation of C_6H_5 and —COO—, but not symmetrical)	+ 61·4	+ 42·5
Diethyl dibenzoyltartrate (symmetrical conjugation)	− 247·1	− 266·0
Diethyl mono-*m*-toluyltartrate	+ 44·0	+ 25·4
Diethyl di-*m*-toluyltartrate	− 306·3	− 325·2

* *Trans. Chem. Soc.*, 1909, **95**, 1578.
† Hilditch, *Zeitsch. physikal. Chem.*, 1911, **77**, 482.
‡ Lowry and Donington, *Trans. Chem. Soc.*, 1903, **85**, 479.
§ Forster and Thornley, *ibid.*, 1909, **95**, 942.
‖ McCrae and Patterson, *Trans. Chem. Soc.*, 1900, **77**, 1096.

Some Attempted Applications of Rotatory Power to Constitution Determination.

Professor Rupe concludes his paper with a résumé of some of his experiments in this field ; the two cases below also indicate that this property may eventually prove of considerable value in this connection to the organic chemist :—

(*a*) *The Structure of Sulphinic Acid Salts, $R \cdot SO_2X$ or $R \cdot SO \cdot OX$?**—The molecular rotatory powers of the brucine and cinchonine salts (in chloroform solution) of the aromatic sulphinic acids studied lie somewhat nearer to the "normal value" of salts of these bases with normal fatty acids than those of the corresponding sulphonic acids, indicating that there is probably less conjugated unsaturation in the sulphinates than the sulphonates, as is expressed in the formulæ $R \cdot SO_2 \cdot X$ and $R \cdot SO_2 \cdot OX$.

The following were the data for the molecular rotations of the benzenesulphinic and benzenesulphonic salts :

	Brucine.	Cinchonine.
"Normal value" (from fatty acids)	— 248	+ 690
Benzenesulphinates	— 106	+ 486
Benzenesulphonates	— 89	+ 408

(*b*) *The Structure of Disulphoxides, $R \cdot SO_2 \cdot S \cdot R$ or $R \cdot SO \cdot SO \cdot R$?*†—The data available for comparison here were mainly those quoted above on the thioderivatives of camphor, together with the rotatory power in aqueous solution of sodium camphoryl-thio-β-sulphonate, $[M]_D + 31°$.

The following rotatory powers were observed for disulphoxides derived from camphor-β-sulpho-compounds in chloroform solution (check determinations being also made in alcohol) :

	$[M]_D$	Difference from Camphor.
Dicamphoryl-β-disulphoxide	— 274	— 204
Methyl camphoryl-β-disulphoxide	+ 116	+ 49
n-Butyl camphoryl-β-disulphoxide	— 72	— 139

The evidence was thus only definite here in the case of the dicamphoryl derivative, where by analogy with the rotatory power of the disulphide the symmetrical formula $C_{10}H_{15}O \cdot SO \cdot SO \cdot C_{10}H_{15}O$ was very clearly indicated.

It may be added that no mutarotation was observed in any of the three compounds.

It is hoped that the above somewhat fragmentary results may help to emphasize the important practical bearing of constitutive influences upon optical activity, of which so admirable an exposition has been given in this discussion by their present foremost exponent, Professor Rupe.

* *Trans. Chem. Soc.*, 1908, **93**, 1620.
† *Ibid.*, 1910, **97**, 1091.

THE ROTATORY POWER OF ASYMMETRIC NITROGEN COMPOUNDS AS AN AID TO THE RECOGNITION OF CHEMICAL CHANGES IN ELECTROLYTES IN NON-IONIZING SOLVENTS.

(TRANSLATED FROM THE GERMAN.)

Professor Dr. E. Wedekind (Strassburg) contributed to the Discussion a Paper on "The Rotatory Power of Asymmetric Nitrogen Compounds as an Aid to the Recognition of Chemical Changes in Electrolytes in Non-Ionizing Solvents."

Aromatic quaternary ammonium halides, which contain a further unsaturated group (allyl or benzyl) when dissolved in chloroform and some other non-ionizing media, are partially dissociated into the corresponding tertiary base and alkylhalide, according to the equation—

$$\mathrm{Ar}.a.b.c.\mathrm{N}.\mathrm{Hal} \rightleftarrows \mathrm{Ar}.a.b.\mathrm{N} + c.\mathrm{Hal}.$$

This dissociation manifests itself in the case of the optically active forms of asymmetric ammonium salts by the loss of activity (the so-called autoracemization of compounds of asymmetric nitrogen).*

The dependence of the dissociation velocity on the nature of the anion and of the kation has been thoroughly investigated † ; also the influence of added substances has been demonstrated ; for example, it has been proved that the dissociation velocity of *d*-propylbenzylmethylphenylammonium iodide in chloroform solution is retarded by the addition of the corresponding nitrate, which itself is not dissociated.‡ This observation could be explained by assuming double decomposition between the two salts, according to the equation—

$$d\text{-}(\mathrm{CH_3})(\mathrm{C_3H_7})(\mathrm{C_7H_7})(\mathrm{C_6H_5})\mathrm{N}\cdot\mathrm{I} + i\text{-}(\mathrm{CH_3})(\mathrm{C_3H_7})(\mathrm{C_7H_7})(\mathrm{C_6H_5})\mathrm{N}\cdot\mathrm{NO_3}$$
$$\rightleftarrows i\text{-}(\mathrm{CH_3})(\mathrm{C_3H_7})(\mathrm{C_7H_7})(\mathrm{C_6H_5})\mathrm{N}\cdot\mathrm{I} + d\text{-}(\mathrm{CH_3})(\mathrm{C_3H_7})(\mathrm{C_7H_7})(\mathrm{C_6H_5})\mathrm{N}\cdot\mathrm{NO_3}.$$

Of the four components which are in equilibrium only the two iodides dissociate, whereas in the polarimetric measurements of the dissociation only the active salt is concerned (*i.e.*, the active nitrate which by itself does not dissociate), which accounts for the retardation in the rate of diminution of rotation. In accordance with this idea, this process comes to a standstill at a certain point, viz., when the whole of the active iodide has been dissociated into tertiary base and alkylhalide ; the remaining rotation is then due to the active nitrate, and consequently the reaction velocity diminishes with the concentration of the added inactive nitrate.

Curiously enough, however, a diminution in the dissociation velocity of

* E. Wedekind, *Zeitschr. f. Elektrochemie*, **12**, 330, 515 [1906] ; E. Wedekind, O. Wedekind, and F. Paschke, *Ber. d. deutsch. chem. Ges.*, **41**, 1029, 2659 [1908] ; cp. H. v. Halban, *Zeitschr. f. Elektrochemie*, **13**, 57 [1907] ; *Ber.*, **41**, 2417 [1908].

† E. Wedekind and F. Paschke, *Ber.*, **43**, 1303 [1910] ; **44**, 1406, 3072 [1911].

‡ E. Wedekind and F. Paschke, *Zeitschr. f. physik. Chem.*, **73**, 118 [1910]. The experiments of v. Halban, referred to in this paper, were carried out by another method (cp. *loc. cit.* **77**, 719 [1911]), which led him to the same explanation as that given by Dauge and myself (*loc. cit.* **82**, 314 [1912]).

the active iodide also follows upon the addition of *active* nitrate, when there can be no question of rearrangement in the above-mentioned way. In order, therefore, to test whether this assumed rearrangement of the two salts in chloroform solution actually takes place, the experiments were varied in such a way as to study the effect of the addition of *inactive iodide* to a solution of *active nitrate*.

In case any measurable diminution in rotatory were detected, it could only be due to the formation of active iodide, *i.e.*, to a reaction occurring in solution between iodide and nitrate; for example—

d-nitrate (opt. stable) + *i*-iodide $\rightleftharpoons$ *d*-iodide (opt. unstable) + *i*-nitrate.

The experiments which are here recorded have confirmed this view. The tables that follow give the data for the observed diminution of rotation in solutions of the mixed salts.

The *d*-methylpropylbenzylphenylammonium nitrate, which was used in all the experiments, had the following properties: Temperature of decomposition = 168–170° $[\alpha]_D$ in chloroform at 25° = + 50·73°. For a time the angle of deviation is constant: within five hours no appreciable change was observed. All further measurements, except those in Experiment V, were carried out in a 2 dm. tube, maintained at 35° by water circulating from a thermostat.

The decomposition-velocity of the pure *d*-iodide can be seen from the following table* :—

EXPERIMENT I.

d-$(CH_3)(C_3H_7)(C_7H_7)(C_6H_5)N \cdot I$ in chloroform (35°).

Min.	α.	$\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$.
	°	
0	1·25	—
14	1·03	0·00600
27	0·86	0·00610
41	0·70	0·00614
57	0·53	0·00653

EXPERIMENT II.

0·3022*g* *d*-$(CH_3)(C_3H_7)(C_7H_7)(C_6H_5)N \cdot NO_3$ + 0·2853*g* $(C_3H_7)_3(CH_3)NI$ in 20 c.c. chloroform at 35°.

Min.	α.	$\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$.
	°	
0	1·30	—
110	0·78	0·00748
126	0·70	0·00445
150	0·63	0·00289
165	0·60	0·00251
235	0·50	0·00177
295	0·43	0·00156
350	0·33	0·00180
410	0·25	0·00171
470	0·20	0·00169

* In this table α_0 is the angle of initial rotation, α_t the angle at time t, $\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$ is the velocity constant of the unimolecular reaction.

On cooling down to the temperature of the room the decomposition becomes scarcely measurable.

Experiment III.

0·3022*g* *d*-$(CH_3)(C_3H_7)(C_7H_7)(C_6H_5)N \cdot NO_3$ + 0·2572*g* $(C_2H_5)_4NI$ in 20 c.c. chloroform at 35° C. after standing for 20 hours at the room temperature.

Min.	α.	$\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$.
	°	
0	0·79	—
40	0·68	0·0016
70	0·61	0·0016
100	0·57	0·0014
130	0·54	0·0013
160	0·52	0·0011
190	0·50	0·00099
310	0·42	0·00088
340	0·38	0·00081

Experiment IV.

0·1511*g* *l*-$(CH_3)(C_3H_7)(C_7H_7)(C_6H_5)N \cdot NO_3$ (1 mol) + 0·2572*g* $(C_2H_5)_4$ NI (2 mols) in 20 c.c. chloroform at 35°.

Min.	α.	$\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$.
	°	
0	— 0·86	—
10	— 0·78	0·00424
20	— 0·72	0·00386
30	— 0·68	0·00336
50	— 0·61	0·00298
130	— 0·37	0·00282

Experiment V.

0·3022*g* *l*-$(CH_3)(C_3H_7)(C_7H_7)(C_6H_5)N \cdot NO_3$ + 0·215*g* $(C_2H_5)(C_7H_7)(HN)$, HBr in chloroform at 45°.

Min.	α.	$\frac{1}{t}\log\frac{\alpha_0}{\alpha_t}$.
	°	
0	— 1·69	—
20	— 1·56	0·00174
40	— 1·48	0·00144
70	— 1·35	0·00139
100	— 1·22	0·00141
130	— 1·13	0·00134
160	— 1·08	0·00122
190	— 1·00	0·00119
310	— 0·72	0·00119

A solution in chloroform of the active nitrate, mixed with the equivalent amount of ethyl iodide, shows no diminution of rotation either at 35° or at 45°, nor have allyl iodide and benzyl bromide any action.

It can be urged then without objection that a rearrangement between two salts in chloroform solution may take place, and can be proved by an optical method on account of the decomposition of the halide that is formed; the reaction can also be followed by titration and by conductivity measurements. The nature of the inactive halide apparently takes no part in the effect, since the salt of a secondary base gives the same result as a quaternary salt.

An increase in the concentration of the inactive halide (Experiment IV: 1 mol active nitrate + 2 mols inactive iodide) increases the velocity constants.

Especially remarkable is the fact that one can deduce from the recorded figures that the rearrangement which occurs between the nitrate and the halides is fairly rapid; for the diminution in rotation, which can only be due to the formation of active iodide, occurs at the commencement almost as rapidly as in the case of the pure active iodide; the retardation which then follows, and which finds expression in the rapid fall in the velocity-constants, must at present be ascribed to the still unexplained peculiar action, previously referred to, of the added salts.

The proof which is hereby furnished, that electrolytes can undergo rearrangement in non-dissociating solvents* without the production of a precipitate or of a gaseous product, should arouse special interest. There can scarcely be any question of a true ionic reaction, for the conductivity of the chloroform solutions of such salts is infinitesimal; nevertheless a transient change could be demonstrated also in this respect after the addition of the halogen salt.

STRASSBURG.
CHEMICAL INSTITUTE OF THE UNIVERSITY,
INORGANIC DEPARTMENT.
May, 1914.

* The same effect was also observed when acetylene tetrachloride was used as solvent.

NOTE ON THE CONDITIONS DETERMINATIVE OF ANOMALOUS DISPERSION.

Professor H. E. Armstrong, F.R.S., and **Mr. E. E. Walker** contributed to the Discussion a "Note on the Conditions Determinative of Anomalous Dispersion."

The conditions under which a liquid substance or a solution may show anomalous dispersion are clearly defined by Tschugaeff in the important and remarkably lucid contribution which he has made to this discussion, but there still remain points of interest to be considered, more particularly from the chemical point of view.

With regard to Patterson's objection to our view, which he expresses by saying, "Limitations of space render it impossible to point out the enormous objections which could immediately be brought against any such idea," we think he might well have found space to state some one objection, even a minute one. It is obviously impossible for us to reply to arguments which are still *in camera*. He unfortunately has given no explanation of the phenomena in terms which the chemist can grasp, though he has been one of the chief workers in the field during twenty years past. Little is to be gained by discussing the use of the terms *normal* and *abnormal* until far more important issues have been settled. We may add that our argument does not depend on our diagram. We must leave it to others and to time to decide as to the value of our method of plotting results; to judge from Pickard's recent publications, however, it appears to have been of service already in his hands.

It will be admitted by most chemists, probably, that anomalous dispersion of the type of that exhibited by ethylic tartrate may be due to the presence of metameric (isodynamic) forms differing in dispersive power, as we have maintained in a recent communication to the Royal Society,* though apparently it is held that two modifications of a substance differing in dispersive power may be produced either (1) by association with the solvent or (2) by polymerization, not merely (3) by passage from one isomeric form to another.

We wish especially to emphasize the fact here that, in order that two normally dispersing substances may produce anomalous dispersion, not only must the two differ in dispersive power, but the one substance must have a rotatory power opposite in sign to that of the other. Bearing in mind the remarkable constancy of the dispersion ratios of the majority of optically active substances under a variety of circumstances which must effect the degree of association of the substance either with itself or with the solvent, we are forced to regard the dispersion ratios as practically independent of these factors unless they are accompanied by a change in chemical type; in no case, we believe, does the combination of two dextrorotatory molecules give rise to one of lævo-rotatory power, whereas many cases are known in which the molecular rotatory power of the resulting compound is very nearly the sum of those of its constituents.

The great majority of normally dispersing substances of similar chemical type have dispersion ratios which are very nearly equal; moreover, the dispersion ratios are but little affected by the nature of the solvent.

* *Proc. Roy. Soc.*, 1913, A, vol. lxxxviii., p. 388.

Thus, of ten substances measured by Pope and Winmill,* two showed variable and anomalous dispersive power, but the dispersion ratio $\frac{\text{Hg green}}{\text{Na yellow}}$ of the remaining eight was the same in all the four solvents used within 3 per cent., and the values in most cases varied to a less extent than this. The same may be said of *d*-Butan-β-ol,† the dispersion ratio $\frac{\text{Hg green}}{\text{Na yellow}}$ of which has been measured in eight different solvents. The maximum difference observed is between the dispersion ratios in benzene and those in acetone (the maximum difference occurred in these two solvents in the case quoted above) and amounts to only 3 per cent.

Even a change in configuration sufficient to invert the sign of the rotation is not necessarily sufficient to alter the dispersion ratios perceptibly ; thus the dispersion ratios of the two isodynamic forms of fructose appear to be equal.‡

Dr. Lowry shows that the dispersion ratio $\frac{\text{Hg violet}}{\text{Hg green}}$ is about 1 per cent. greater in the case of α-methylglucoside than in that of the β-isomeride.§ Supposing α- and β-fructose were to differ by this quantity, the dispersive power of the solution would be anomalous if conditions could be found to shift the equilibrium sufficiently in the α-direction (about 92 per cent. α-fructose), but only when the observed specific rotatory power lay between −0° ·05 and zero—a range scarcely within the limits of ordinary observation. To produce anomalous dispersion over a range so great as that observed in the case of the ethereal salts of tartaric acid (13°), Pickard and Kenyon's ethereal salts of secondary alcohol (3°) or of *o*-nitrobenzoyl-*l*-tetrahydroroquinaldine (90°), the differences between the dispersion ratios of the two components must be very considerable.

In applying the graphical method we have suggested of correlating the rotatory power and dispersive ratios of substances the dispersive power of which varies considerably, according to the solvent, the concentration or the temperature, the specific rotatory powers found in light of one refrangibility either in different solutions or at different temperatures, etc., are plotted on a sloping line, the ordinates representing the specific rotatory power under one or other condition, the rotations produced in light of other refrangibilities being plotted on the corresponding ordinates.

It is found generally that the points lie on a straight line : the diagram may be regarded as part of a rotation-composition diagram (see Diagram), in which the composition is represented (assuming that the variations are produced by alterations in the equilibrium between two isodynamic forms) to an unknown scale by the abscissæ. The diagram so obtained may be called the characteristic diagram of the substance.

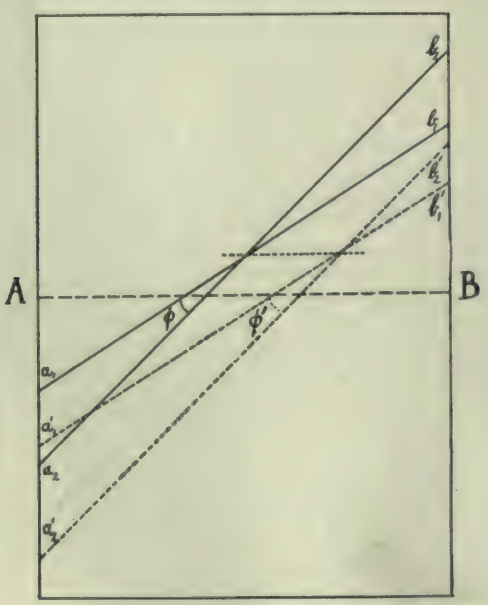
Pickard and Kenyon have pointed out that a whole series of nearly related optically active compounds have the same characteristic diagram: the diagram may therefore be characteristic of a whole group of compounds, such as the various ethereal salts of an optically active alcohol, rather than of a single compound. They regard this result as proof of the existence of close relationships between the rotatory powers of the various derivatives.‖

It is worth while to inquire what numerical relationships between the rotatory powers of a series of substances would account for the coincidence

* *J.C.S.*, 1912, p. 2309.
† Pickard and Kenyon, *J.C.S.*, 1914, p. 883.
‡ Cf. *Proc. Royal Soc.*, A., vol. lxxxviii., p. 393.
§ Lowry and Abram, *supra*, p. 105.
‖ *J.C.S.*, 1914, p. 846.

of their characteristic diagrams. Suppose that A and B are two isodynamic substances and that their rotatory powers are a_1 and b_1 respectively in light of one refrangibility and a_2 and b_2 in another, and let A′ and B′ be another pair of isodynamic substances related to one another chemically as are A and B and let the corresponding rotatory powers be a'_1, a'_2 and b'_1, b'_2; in order that the characteristic diagram of these two pairs of isodynamic substances may be strictly superimposable, the angle ϕ must be equal to the angle ϕ', and the two pairs of lines must cross each other when the rotatory power of each pair is the same.

The simplest relationship between the rotatory powers of the four



substances concerned that would fulfil the conditions named would be when—

$$b_1 - a_1 = b_1 - a_1 \text{ and } -b_2 a_2 = b'_2 - a'_2.$$

In other words, the difference between the rotatory powers of the isodynamic substances A and B must be equal to that between A′ and B′. Such relationships between the rotatory powers of isodynamic substances and their derivatives are not unknown: thus C. S. Hudson has shown* that the difference between the molecular rotatory powers of the two isodynamic forms of various reducing sugars is a constant quantity. This relationship has also been found to hold in the case of various methylated derivatives of glucose by Irvine and others.† An exactly similar relationship between the rotatory powers of the two isodynamic forms would account for the facts observed by Pickard and Kenyon.

* *Jour. Amer. Chem. Soc.*, 1909, 31, 66.

† *J.C.S.*, 103, 1386; 105, 564.

DISCUSSION.

Professor Percy F. Frankland, F.R.S., who presided over the evening session, opened the general discussion which followed the reading of the Papers.

It has given me great pleasure to preside to-night. It is the first occasion on which I have attended a meeting of the Faraday Society, and it reminds me of the fact that I am doubtless the only person in this room who has had the privilege of seeing Faraday, for I can well remember having once sat upon his knee when I was of very tender years in the early sixties of the last century.

The Faraday Society is to be congratulated on having brought together this series of communications, and I hope that a valuable discussion will follow. Unfortunately, the time left for the discussion is limited to less than an hour. The discussion must be briefer than many of you may desire, and my own remarks will be especially so, as I have come more as a learner than to impart views of my own.

The communications cover a very wide field and deal with optical activity from many different points of view, both physical and chemical.

The chief novelty which has appeared is the stress laid by several of the authors on the determination of rotatory dispersion, and I imagine the discussion will be devoted more particularly to this question.

We must all admire the unremitting efforts made by Dr. Lowry and his coadjutors to overcome the experimental difficulties attending the determination of rotatory dispersion over such a great range of the spectrum visible and invisible.

I congratulate Dr. Patterson on the great service he has rendered to the subject of optical activity by his comprehensive experiments on rotation in solution, which is a subject that has repelled most experimenters because of the enormous amount of material that must be collected before any general conclusions can be arrived at. He has shown that each solvent has almost a specific action on a variety of active compounds, and this in itself must be regarded as a most important achievement, inasmuch as it has introduced some order into what was before a bewildering mass of disconnected observations.

It seems to me that the really characteristic thing about the relationship between optical activity and wave-length is that when a change in optical activity is brought about by any given agency, the effect produced is the greater the smaller the wave-length. Therefore, if there is any agency such as rise of temperature which causes the rotation to increase or decrease as the case may be, the greatest change will be effected in the case of the light with the smallest wave-length. The chief agencies effecting change of rotation are substitution, alteration of temperature, action of a solvent, and dilution. If in any of these changes the curve of rotatory power for monochromatic light passes through a maximum and through a minimum, it follows that somewhere between these extremes there must be anomalous dispersion. There would appear also to be a phenomenon which I would call *spurious anomalous dispersion* and which is occasioned by the curve crossing the zero line, for the position of the zero line seems to me to be arbitrary.

Professor Tschugaeff in his paper has given a clear and most useful classi-

fication of the different types of anomalous dispersion, and it is especially interesting that he has found distance of the chromophors from the asymmetric carbon atom to exercise an important influence on the rotatory dispersions associated with Cotton's phenomenon. We cannot fail to be impressed with the ingenuity of Professor Armstrong's characteristic diagrams, which seem to be a sort of *multum in parvo*, as they are capable of compressing into a small space a large amount of information, as shown by Dr. Pickard.

It is obviously quite possible to explain cases of anomalous dispersion by assuming a mixture of two different substances, but it seems to me that it should only be resorted to when other explanations have been removed by a process of exhaustion.

With regard to the abnormality in the rotatory dispersion of methylnaphthyl carbinol when in the superfused condition, I should like to point out that processes of association might take place in this case which would lead to great complications.

We have been told that the use of one kind of light has led to only disappointing results, but it seems to me that there has been great actual progress made by this means and that the progress in the future will be much slower owing to the greater labour and experimental difficulties in using light of different wave-lengths. Moreover, it seems to me that anomalous dispersion may be postulated from the results obtained with monochromatic light, for if we get a curve with a maximum or a minimum when using monochromatic light, we know that anomalous dispersion will occur. This anomalous dispersion may be due to the presence of two different substances or to the *dominance* of different groups under different conditions of temperature, etc. We get a clear idea of what is meant by the dominance of one group by means of Guye's expression for the "product of asymmetry."

As there seems to be a tendency to overlook and belittle the results which have been obtained by the use of monochromatic light, I would mention a few of the achievements that stand to the credit of this mode of study, such as (*a*) recognition in homologous series of the tendency of the chain to return upon itself at certain fixed points; (*b*) indications of the association of optically active liquids and the formation of labile compounds between the solvent and the active solute; (*c*) the effect of unsaturation, as so fully elaborated by Rupe and by Hilditch, *d*) position isomerism, (*e*) distance from the asymmetric centre, (*f*) superposition of the effects of several centres of activity in the molecule, (*g*) the comparative influence of aromatic and fatty groups, and (*h*) above all the discovery of the Walden inversion, which has thrown such important light on the mechanism of substitution.

All these results have been arrived at by the antiquated and obsolete method of using monochromatic light!

Dr. T. S. Patterson: I may perhaps explain that by the phrase "the potentialities of the asymmetric carbon atom" to which Professor Armstrong in his opening remarks referred, I mean simply the dominance, at different temperatures, of one or other of the four groups to which the asymmetric atom is attached; whilst by the further phrase "the most simple physical conception of those intermolecular forces to which liquefaction is due," I wish to suggest merely an attraction between the molecules of the solvent producing an effect analogous to pressure in the liquid; this internal pressure would diminish as the temperature rises. These seem very simple and indeed obvious ideas, and they appear to me to be sufficient to account for nearly all the phenomena of rotation-change with which we are acquainted.

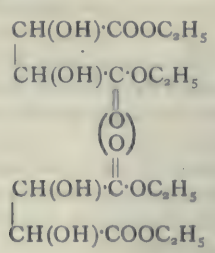
Because the rotation-dispersion curve for ethyl tartrate can be represented by an expression containing two terms, Dr. Lowry has suggested the presence in the ester of two isomerides. It is clear, however, that such an argument can carry no weight, for each of these terms may be replaced by two others, each of these again by two others and so on, in which way evidence could be obtained in favour of the existence of an infinite number of isomerides.

Unlike Professor McKenzie, I incline to the view that the work which has been done in recent years on spontaneously active compounds of very different type appears to show that they all behave in a surprisingly similar manner with change of external conditions, provided their behaviour be regarded from a sufficiently comprehensive point of view.

Dr. A. McKenzie : We all admire the beautiful apparatus exhibited this evening by Dr. Lowry and Mr. Abram and recognize the extent to which work on rotatory dispersion has been facilitated by the methods now at our disposal. At the same time, in this discussion where the importance of the measurement of rotatory dispersion has been emphasized, it is not out of place to emphasize, as the Chairman has already done, the great advances in stereochemistry which have been rendered possible by the use of sodium salts as the source of light.

The difficulty of arriving at generalizations on the relationship between constitution and rotatory power is great, since the various workers in the field have confined their valuable observations mainly to derivatives of one type, *e.g.* glycerates, tartrates (Frankland), lactates (Purdie), tartrates (Patterson), menthyl esters (Rupe), etc.

It seems to me that the variation of optical activity undergone by a compound with the alteration of temperature may be due to some such cause as the following. Take the case of ethyl *d*-tartrate with two ketonic centres. In virtue of the reactivity of the carbonyl groups, we may imagine a labile complex of this type to be formed :



the two molecules of ethyl tartrate are united by a linking which is easily severed. This complex may in turn add on additional molecules of ester. It is suggested that polymerization of this nature cannot be detected by the ordinary physical methods for determining molecular weight but the number and nature of the complexes alter with variation of temperature and the change in rotatory power is the result of such an alteration.

The conception of the existence of tautomeric forms as an explanation of anomalous rotatory dispersion will be rendered more plausible when the isolation of such forms has been effected.

Mr. J. Kenyon : Quite recently I have prepared two further series of optically active esters and investigated the effect of temperature on their rotatory powers over a range of nearly 200° C.

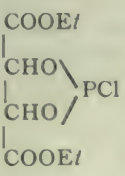
Dr. Patterson's view is that the rotation values of an optically active

substance under all conditions can be plotted on one periodic curve. The rotation values of these particular esters vary to only a slight extent over a wide range of temperature and furthermore lie on a series of straight lines. It would therefore seem that the curves which would be necessary in order to fit straight lines on them would have to be very large ones indeed.

With regard to the remarks of Professor Frankland about the anomalous rotation of methyl-*a*-naphthyl carbinol being measured whilst the substance is under peculiar physical conditions, I should like to point out that there is no break in the continuity of the temperature-rotation curve of it when this is continued beyond the temperature of normal melting-point into the region of superfusion.

Mr. G. W. Clough : With regard to the use by Professor Grossmann of phosphorus trichloride as a solvent for the esters of tartaric and malic acids, I might mention that this chloride rapidly attacks the esters in question. In the case of ethyl tartrate there is a brisk evolution of hydrogen chloride ; on removing the excess of phosphorus trichloride at the ordinary temperature and distilling the residue under diminished pressure, the distillate contains phosphorus and chlorine, and on hydrolysis with water gives HCl,H_3PO_3, alcohol and tartaric acid.

The compound is probably :



and it gives a_D—120° (circ.) ($l = 0{\cdot}5$ dm.). It is unfortunate that Professor Grossmann has tabulated his results as the rotations of the esters in phosphorus trichloride. So is the fact that he has called the change in rotation with the time "mutarotation."

Dr. R. H. Pickard : The existence of two isomerides in a supposed homogeneous substance as an explanation of anomalous dispersion may not have definite chemical evidence in support of it ; but that also holds good for the alternative suggestions.

Thus there appears to be no authenticated case in which the polymerization of a compound has been shown to affect its rotatory power.

Dr. T. M. Lowry : It is necessary to emphasize the fact that a dispersion-curve which appears normal to the eye is not necessarily *simple*, and must not be described as such until it has been tested. This can be done by plotting $\frac{1}{a}$ against λ^2, when a simple dispersion will give a straight line, whilst a complex dispersion will give a curve. The test is quite as simple as the use of Armstrong and Walker's "characteristic diagram," and I hope it will be adopted generally.

Even before this test has been made, any substance for which a_{4359}/a_{5461} was less than about 1·630 was open to suspicion, as this appeared to be almost the minimum value of this ratio for cases of simple rotatory dispersion, The explanation was that all organic compounds appeared to have a strong absorption band at a wave-length not less than 1,100 A.U., and a smaller ratio could only be produced by introducing a second term into the equation. Even if the absorption-band were removed to infinity, as in Biot's equation, the ratio could only fall to $(5461)^2 \div (4359)^2 = 1{\cdot}57$.

Professor Frankland had suggested that the line of zero-rotation was arbitrary and had no special significance. This was quite true from the chemical point of view, where a gradual change of structure might cause a progressive change of rotation passing through a zero-value, though even there chemists had been in the habit of attaching special significance to the presence or absence of optical rotatory power in a compound. From the physical point of view, however, the line of zero-rotation was a fundamental axis which differed from every other line that could be drawn, *e.g.* it was the asymptote to which all curves of rotatory dispersion ultimately approached as the wave-length increased. Again, it was quite easy for a substance to have a zero-rotation for all wave-lengths, and the temperature-rotation curves for all wave-lengths might easily intersect on this axis; but for a substance to produce a constant rotation throughout the spectrum, other than on the axis of zero-rotation, would be nothing less than a miracle.

Mr. Patterson and Professor Frankland had attempted to account for anomalous rotatory dispersion as due to the drift of the temperature-rotation curves with change of wave-length. This involved a transposition of cause and effect which could not be maintained. The dispersion-curves were fundamental. In plotting them nothing was altered but the wave-length of the light that was used to test the properties of the substance; the substance itself remained unchanged and in the same condition throughout. It was for this reason that the dispersion-curves lent themselves so readily to mathematical treatment. The temperature-rotation curves, on the other hand, included all the secondary changes produced by rise of temperature in a liquid, such as depolymerization, dissociation of complexes of solvent and solute, etc. Under these conditions simplicity of form could scarcely be expected, nor could the significance of the curves be understood until the various physical and chemical factors which they involved had been disentangled.

Although anomalous rotatory dispersion might be produced in various ways, it was probably due in most cases to the presence in the liquid of two or more varieties of optically active molecules. The advocates of this view had been challenged to produce evidence in favour of it. This could easily be done. On the one hand, nitrocamphor, which was known to exist in two isodynamic forms, had been found to give rise to anomalous rotatory dispersion when dissolved in acetone. On the other hand, ethyl tartrate, the traditional example of anomalous rotatory dispersion, had been proved to be a mixture, which could be fractionated by distillation in a vacuum; Mr. Abram had obtained fractions ranging in rotatory power from 5° to 15°. These readings were taken with violet light and with 6 dm. columns of the liquid; the variations with green light were relatively insignificant.

Mr. Clough objected to the name mutarotation being applied to cases where there is an interaction between solvent and solute. As the author of the term, the speaker saw no objection to this. The word was introduced to describe change of rotation with time and had been applied equally to the hydrolysis of gluconic lactone and to the interconversion of the isodynamic forms of glucose.

Mr. Hilditch gives the impression that the measurement of rotatory dispersion is only important in the case of substances which show marked anomalies. This is only partially true. The discovery of the law of simple rotatory dispersion makes it possible for the first time to separate completely the factors of rotation and of dispersion. This does not matter much at present, because the study of the influence of chemical constitution on optical rotatory power is still on a semi-qualitative basis: if at any time it should develop in

such a way that the actual numerical values of the rotations have to be taken into account, it will be found that measurements of dispersion are even of more value when the dispersion is simple than when it is complex.

Professor H. Grossmann : I cannot agree with Professor Frankland if he says that work with a single kind of light is sufficient. Much has been discovered by this means, but there are many instances where wrong conclusions have been arrived at through the use of a single kind of light, notably in the case of Beckmann's supposed interconversion of *d*- and *l*-menthone.

RECORDING PYROMETERS

By CHAS. R. DARLING, A.R.C.Sc.I., F.I.C.

(*A Paper read before the Faraday Society, Wednesday, April 22, 1914,* Professor Alfred W. Porter, F.R.S., *in the Chair.*)

The first successful attempt to secure an automatic record of high temperatures was made by Le Chatelier in 1887, in conjunction with a thermoelectric pyrometer. A spot of light, reflected from the mirror galvanometer used as indicator, was directed upon a sensitized plate, and by this means a photographic record of changes in temperature was secured. The same method was adopted later by Roberts-Austen for the work of the Alloys Research Committee of the Institution of Mechanical Engineers, and as a result of the early labours of this Committee the utility of recording pyrometers was firmly established. In 1898 Callendar introduced his recorder for use with resistance pyrometers, which possessed the great advantage of furnishing an ink record on a paper chart; and this was followed in 1900 by the intermittent contact recorder for thermoelectric pyrometers, designed by the firm of Siemens-Halske, which enabled ink records to be obtained with this class of instruments also. The remarkable growth of our knowledge of high-temperature measurement during recent years, together with the recognition of the value of pyrometers in the industries, has resulted in the introduction of numerous types of recorder, designed mainly to meet industrial requirements. The main purpose of this paper is to discuss the advantages of the more recent of these appliances, more particularly with regard to practical furnace control, and to indicate possible future developments in this connection.

Before proceeding to a description of actual recorders, it will be necessary to consider the modern trend of opinion with respect to the utility of the types of pyrometer to which recorders may be applied. As an instrument for the purposes of research, or for accurate work under steady conditions, when the temperature does not exceed 1,000° C., the resistance pyrometer is undoubtedly the best. Under the usual circumstances prevailing in industrial processes, however, the superior precision of which this pyrometer is capable is of no advantage; and hence at the present time the thermoelectric pyrometer, being cheaper and more easily managed, is preferred for commercial use for temperatures up to about 1,200° C. Until quite recently pyrometers of this type were made exclusively with junctions of platinum and platinum-rhodium or platinum-iridium; but these costly metals are now being superseded to a large extent by base-metal couples, such as nickel and carbon, two nickel-chrome alloys, or two iron-nickel alloys. As base-metal couples yield an e.m.f. several times as great as those of the platinum series, it is possible to modify indicators and recorders so as to take advantage of the increased power available. For temperatures above 1,200° C. it is now customary to use radiation pyrometers, of the type devised by Féry, Foster, or Thwing; and as the thermoelectric principle is utilized in these instruments, the class

of recorder suitable for thermoelectric pyrometers may be adapted for use with radiation pyrometers. Other methods of measuring high temperatures do not lend themselves to the production of automatic records, and hence two types only come up for consideration—the resistance and the thermoelectric.

The requirements of modern furnace practice render the following qualifications desirable in any recorder :

1. The readings should be accurate within the limit desired.

2. The recorder should be dust-proof and strongly built, and not seriously affected by vibrations.

3. It should be capable of taking several records simultaneously on the same chart.

4. It should require the minimum of skilled supervision and upkeep. If used for the purpose of research, under the conditions usually prevailing in a laboratory, the last three qualifications are not of such importance. It is necessary, in all considerations in relation to recorders, to keep in mind the conditions of use, as the successful design of an instrument depends largely upon other factors than mere accuracy of reading. Some of the latest examples of recorders will now be considered from the standpoint of the qualifications mentioned.

Thermoelectric Recorders.

The feature common to most thermoelectric recorders in which the registration takes the form of an ink mark on a paper chart, is the periodic depression of a bar on to the galvanometer needle or pointer, causing it to mark its position on the chart. The paper is moved at a definite speed beneath the pointer ; and it is divided by vertical lines representing time, and horizontal lines to show temperatures. Owing to the small force available for moving the pointer, it is not advisable—even with base-metals junctions—to permit the pointer or its attachment to be in continuous contact with the paper, as errors due to friction would then arise. In designing these instruments, therefore, the presser-bar must be arranged to descend and then to leave the pointer free for a sufficient time to enable a steady position to be attained. An intermittent or dotted record results, but with a slow paper feed the separate dots nearly blend into a continuous line. The application of this general method, however, differs in the various recorders made, as will be seen from the descriptions which follow.

In the Siemens-Halske recorder (Fig. 1) B is the presser-bar, which is caused by clockwork to descend on to the pointer, which carries near its extremity a short stylus. The chart is moved by clockwork over a typewriter ribbon, and is made of transparent paper. At each descent of the bar the stylus presses the chart on to the ribbon, forming a dot below which is visible above. A permanent temperature scale is provided beneath the pointer, so that the temperature at any moment may be read without consulting the chart. The horizontal divisions on the paper are circular in shape, and must be drawn with a radius equal to the distance between the galvanometer pivots or suspension and the stylus. For a scale divided from 0° to 1,200° C. an accuracy of 5° to 10° is possible—provided the attached pyrometer be correctly managed. For factory use a dust-proof cover is provided, and the general build is such that a little rough handling is not detrimental. Skilled oversight is not necessary ; and by the attachment of an automatic switch several records may be taken simultaneously of the temperatures of different furnaces A typical circuit, showing five pyrometers, is shown in Fig. 2,

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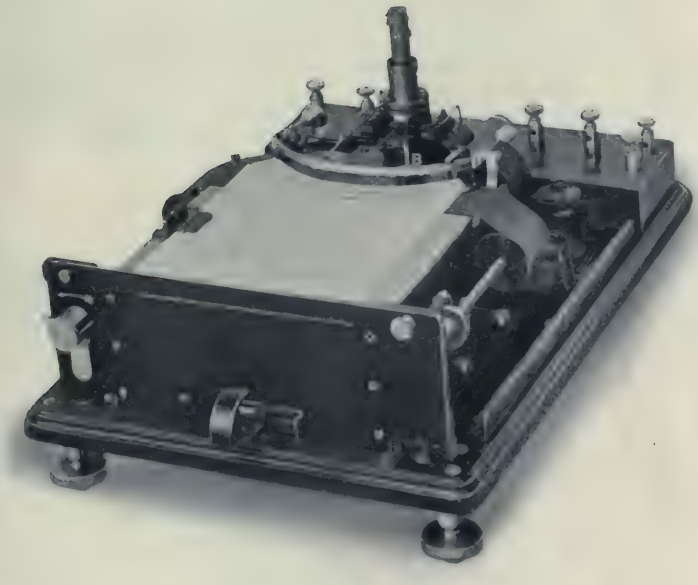

FIG. 1.

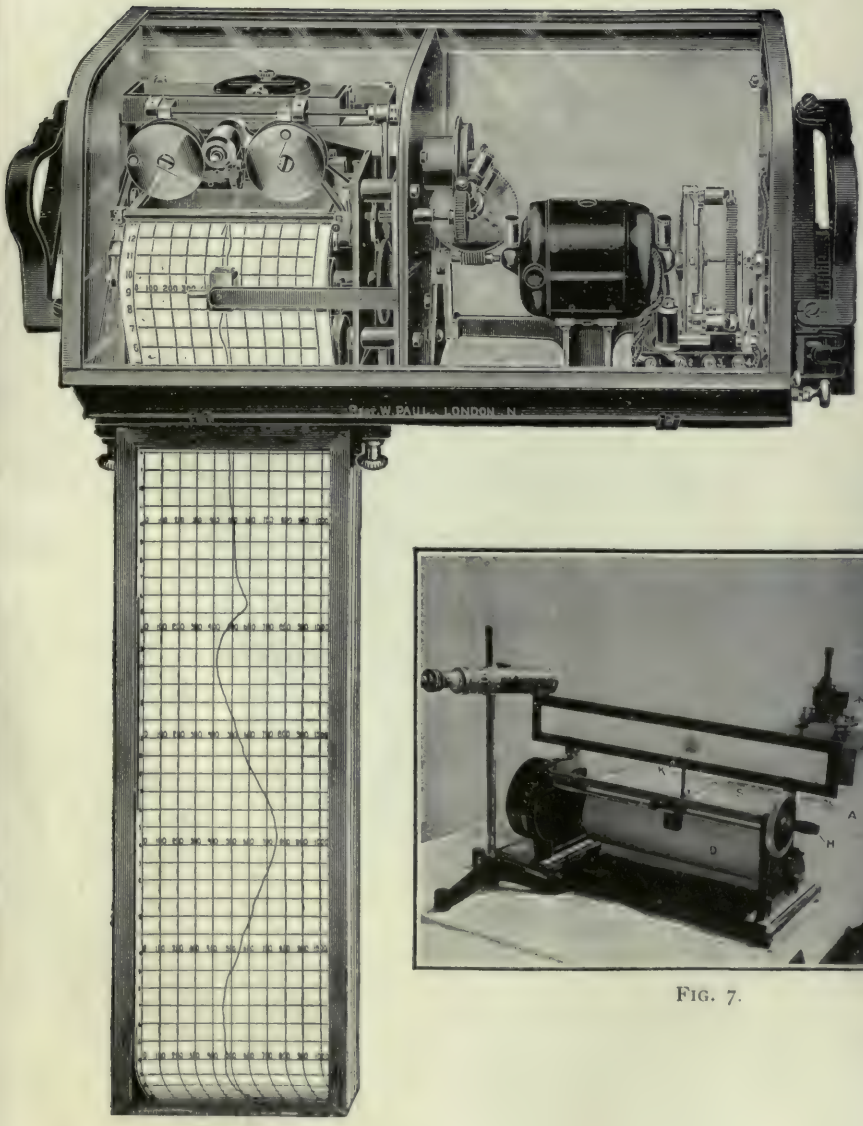

FIG 5.

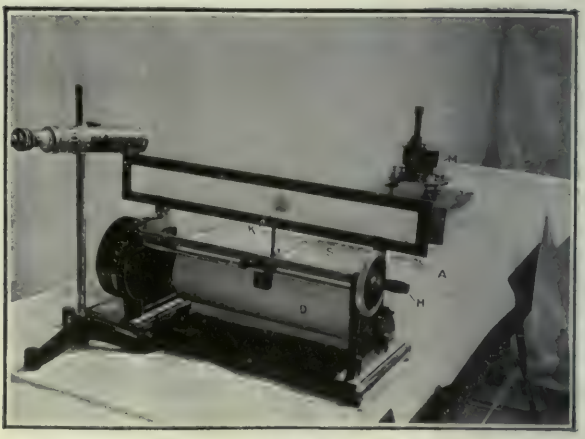

FIG. 7.

where S is the switch, operated by the battery B_2. If the temperatures of each furnace were nearly alike, a confusion of the separate records might result, and in such case the stylus is replaced by a small wheel, on the circumference of which are marked symbols corresponding to the different pyrometers. This wheel is made, by a special mechanism, to rotate synchronously with the action of the switch, so that the correct symbol is stamped on the chart. Evidently the same continuity of the record cannot be secured when multiple records are taken, but unless the fluctuations in any furnace are very rapid, the points will be sufficiently close to give the required information. An attachment is sometimes added whereby the pointer, on passing an assigned temperature, completes on depression a circuit containing an alarm-bell, and thus gives a warning to the fireman—a most useful contrivance in cases where overheating might cause a serious financial loss.

The Leskole recorder differs in several particulars from the foregoing. The end of the pointer is bent at a right angle, and moves over a paper chart wound over a drum, which is rotated by clockwork. The presser-bar is operated by an electromagnet, which is furnished with current from a battery, and the inking device is simple and novel. At definite intervals the battery is switched by clockwork into the pyrometer circuit through a suitable

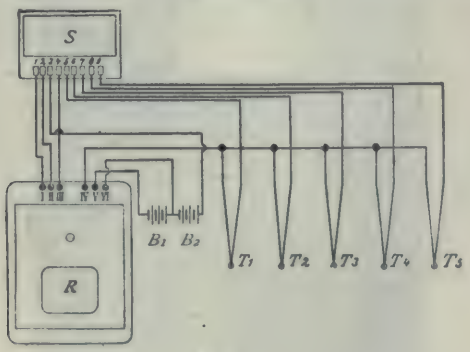

FIG. 2.

resistance, so that the pointer moves over to the extremity of the scale. The bar then descends and presses the end of the pointer on to an inked pad. The presser is then released, and the connection of the battery with the pyrometer broken, so that the pointer acquires its correct position. The bar again descends, and the drop of ink on the end of the pointer is then transferred to the chart. This mode of procedure is quite effective, and simplifies the inking mechanism. It would be difficult to use the instrument, however, for simultaneous records of several pyrometers; but with this limitation it fulfils the conditions imposed by workshop practice.

Foster's recorder (Fig. 3) is designed for use with base-metal couples of the nickel-chromium type, known as Hoskin's alloys, which yield an e.m.f. about five times as large as a platinum-rhodioplatinum couple. The force available in this case enables the coil of the galvanometer to be pivoted in a horizontal position, the pointer being vertical, and yet to be sufficiently sensitive. The chart is mounted on a vertical plate which rotates on its axis, the time ordinates taking the form of concentric circles, which are cut at an angle by the temperature ordinates. At the terminus of the pointer is placed a small capillary tube, fitted with an inked wick, which, when pressed upon

the chart, makes a mark. The presser-bar is curved to the same radius as the pointer, and carries a pad wetted with ink, so that at each depression the supply of ink to the wick is replenished by an amount equal to that imparted to the chart. This recorder is sometimes fitted with special contacts, so that when the correct temperature exists an electric lamp with a white bulb remains lighted ; whereas when too low or too high a green or red lamp is lit up, and an alarm thus given. Such an addition involves the use of a relay circuit, but is advisable in cases where expensive articles might suffer if overheated. It might be modified to permit of several simultaneous records being taken ; and possesses the advantage that the whole chart is visible at any time. On the other hand, the circular co-ordinates may be accounted a drawback by some, as not being quite so familiar to read as charts in which the lines are straight. Robust construction is a feature of this recorder.

The Thread recorder, made by the Cambridge Scientific Instrument Company, enables charts divided into lines at right angles to be used, and as a

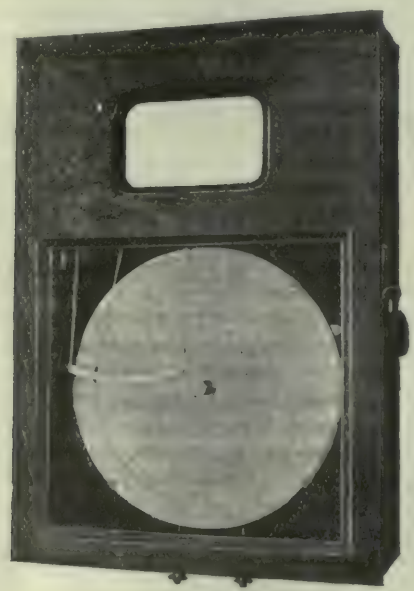

FIG. 3.

suspended-coil galvanometer is employed, a high degree of sensitiveness is possible. In this instrument the pointer is depressed by a horizontal bar on to an inked thread, placed parallel to the axis of the rotating drum which carries the chart, the thread touching the paper at each depression. By this means the tangential instead of the radial movements of the pointer are recorded, and hence the temperature lines are horizontal ; the time lines being vertical. In taking two records simultaneously, the galvanometer may be duplicated and the drum extended, as shown in Fig. 4. Multiple records may be secured by the use of a suitable automatic switch. It might be suspected that the restitution of the pointer to its correct position after release might occupy a considerable time ; such is not the case, however, a few seconds sufficing to effect this. Nor is the instrument unduly affected by the vibrations prevalent in workshops ; and when fitted with a dust-proof cover this recorder satisfies all the necessary conditions. It is peculiarly suited,

owing to its sensitive character, for use with radiation pyrometers, although owing to the introduction of the zinc-antimony receiving junction in these pyrometers, pivoted recorders may also be used. The various movements of the Thread recorder are actuated by clockwork. The use of a scale-control —one of the recent developments of thermoelectric pyrometry—might suitably be described here. When, as in the case of the Thread recorder, a full-scale deflection may be obtained with say 400° C., a closer reading could be secured between 500° and 900° if the starting-point of the scale were 500° instead of 0°, as the space representing a given temperature interval would then be more than doubled. To accomplish this, the pyrometer is made part of an adjustable potentiometer circuit, so that its e.m.f. is opposed to a potential difference between two points of the circuit. This p.d. may be regulated so that at 500° or any other desired temperature the pointer will be at balance on the zero of the scale. An increase in temperature in the pyrometer, causing an increased e.m.f., results in a movement of the pointer over the scale, the whole of which is then utilized for the interval of temperature to be measured. This device may be used to great advantage with the Thread

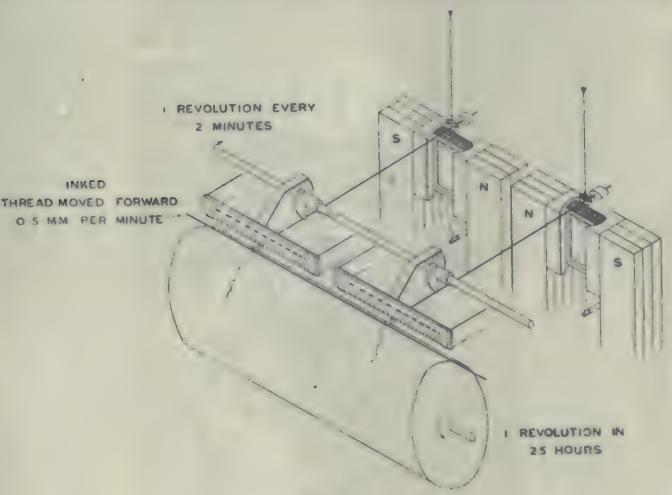

FIG. 4.

recorder when very exact readings are required, and are rendered possible by the conditions prevailing in the furnace.

In the recorders previously described, the motive power is furnished either by clockwork or batteries operating electromagnets. R. W. Paul has recently devised an instrument in which all the moving parts are actuated by a motor driven with power from the mains. This recorder is shown in Fig. 5. The motor is furnished with a special type of governor to ensure constant speed, and is connected by suitable gearing to the mechanisms moving the chart, presser-bar, and inking ribbon, provision being made to vary the speeds of these movements by changing the gear. The galvanometer is of unipivot pattern, and the pointer is pressed at intervals on to a typewriter ribbon which lies above the chart. Immediately beneath the ribbon is placed a thin metal rod over which the paper passes, and the result of the contact is to produce a small dot. As in the Thread recorder, the chart is divided into rectilinear co-ordinates, the ribbon in this case serving the same purpose as the thread in the former instrument. The lower part

of the recorder is prolonged so as to display a considerable length of the chart, which is in the form of a roll, and is drawn forward by the mechanism. When two records are taken simultaneously the ribbon consists of two strips, one moistened with black ink, and the other with red ; and it is arranged that each strip in turn is over the thin rod on to which the pointer is pressed, so that the records appear in separate colours. This recorder can also be arranged for multiple records, or fitted with a scale-control. With a view to workshop use, all the covers are fitted with faced metal joints, which are much better for keeping out dust than wooden ones. A further useful feature is that the various units in the recorder—galvanometer, motor, feed and record mechanism, and reducing gear, are all separate and interchangeable. By introducing a suitably divided chart this recorder will also serve for a radiation pyrometer ; or, as will be shown later, for a resistance pyrometer.

The Leeds and Northrup Company, of Philadelphia, has recently introduced a recorder which it is expected will soon be available in the country. As in Paul's recorder, all the mechanism is motor driven ; but the other arrangements are entirely distinct. Instead of measuring the deflection of

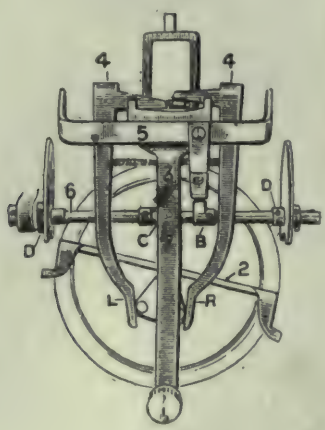

FIG. 6.

the pointer, a zero deflection method is used. The pyrometer forms part of a potentiometer circuit, and the function of the mechanism is to oppose an e.m.f. equal to that of the pyrometer, from which the temperature is known. This principle has the advantage that the measurement is independent of the resistance of the leads, and is capable of great accuracy. The manner in which the adjustment of the opposing e.m.f. is controlled may be understood from Fig. 6, in which the galvanometer coil is shown at the top of the figure. The shaft from the motor carries four cams, B, C, D, D, and at each revolution the cam B raises the bar (5) so as to press it against an arm attached to the galvanometer coil. At the same moment the cam C pushes against the bar (3), and thereby releases a clutch (2) from the disc beneath. As shown, the boom from the coil is to the right of the central position, and is gripped between a bar (5) and the lever (4) when the former rises, causing an angular movement of the clutch-arm (2). As the rotation continues the cam C leaves the bar (3), which then springs back and engages the clutch on the disc. The cam D then descends and presses on the projection of

the clutch-arm to the left, causing the disc to rotate. The movement of the disc is conveyed to an arm which moves over the slide wire of the potentiometer ; and this movement continues until the galvanometer boom is in the central or zero position, when neither of the levers 4, 4 is gripped, and consequently the disc is not fed in either direction. If the boom swing to the left, the movement of the disc will evidently be in the converse direction to that described.

In this recorder considerable power is available to drive printing or other mechanisms. The arm moving over the potentiometer wire carries a pen which marks the moving chart, or, when several records are taken simultaneously, a stamping machine is used which impresses the number of the pyrometer on the chart. The same galvanometer mechanism serves also for use with resistance pyrometers.

The foregoing are typical examples of modern thermoelectric recorders, and show the great progress made during recent years in this branch of pyrometry. It should be mentioned that the photographic recorder, as used by Roberts-Austen, is still employed, having been rendered suitable for workshop purposes by the White Instrument Company. It is too well known to need description.

Before leaving this portion of the subject, reference may be made to the semi-automatic recorder due to Brearley, in which the observer traces in ink on the chart the movements of the spot of light from a mirror galvanometer. The apparatus is shown in Fig. 7 (facing p. 141). The movements of the spot of light due to the changing temperature are followed by turning a handle so as to keep a moving pointer at the centre of the spot. The other end of the pointer carries a pen which is kept in contact with a rotating chart, to which the deflections are thus transferred. This instrument is of great use in obtaining records of recalescence points, etc., in which an open temperature scale is desired.

Resistance Recorders.

When work of precision is being conducted below 1,000° C., resistance pyrometers and recorders are far more suitable than any other type. Extreme precision, however, is not required nor attainable in many furnace operations, and hence the use of resistance recorders industrially is usually restricted to work of a special character. Callendar's recorder, in which the automatic adjustment of a Wheatstone bridge circuit is effected by mechanisms set in motion by the completion of relay circuits by an arm from the galvanometer, has been in use for some years, and needs no detailed description. It possesses the great advantage that the whole width of the chart may be used for an interval as small as 5°, or as large as 1,000°. In the hands of an observer skilled in the use of instruments, this recorder may often with advantage be employed in connection with workshop operations. It is inadvisable, however, to entrust it to an untrained workman ; and this fact, coupled with its high cost as compared with thermoelectric recorders, has restricted its general adoption.

A modified form of Callendar's recorder, built on more robust lines, was introduced in 1909 by the Leeds and Northrup Company, and has been successfully used in America. In the new recorder made by this firm, the mechanism shown in Fig. 6 is used to operate a resistance in one arm of a Wheatstone bridge, until the resistance of the pyrometer is balanced and the galvanometer boom is at zero position. The movements of an arm which moves over the balancing resistance are marked on the chart ; and,

as in the case of thermoelectric pyrometers, several simultaneous records may be taken.

The use of a single recorder for either thermoelectric or resistance pyrometers is of great advantage when both types are in use, and various devices have been adopted to secure this end. In Paul's recorder the galvanometer is replaced by a Harris indicator—a special form of ohmmeter which gives direct temperature readings—and a chart prepared for resistance pyrometers inserted. Other makers supply a Wheatstone bridge arrangement in which the pyrometer is balanced at o°, the galvanometer pointer then being at zero on the scale. On heating the pyrometer its resistance increases, and the balance is lost, so that the pointer moves over the scale by an amount depending upon the increase in resistance. The chart is divided to read temperatures corresponding to the position of the pointer. Such an arrangement is of the same order of accuracy as that obtained with a thermoelectric pyrometer covering the same range.

Special Uses of Recording Pyrometers.

Apart from the obvious advantages resulting from the possession of a full knowledge of the condition of a furnace at all times, there is now a prospect of controlling the heat supply through the agency of the recorder. This is rendered more probable from the fact that in the latest instruments a considerable power is available, which, under the control of the recorder, might be applied to regulating the resistance of an electric furnace, the gas supply in a gas-fired furnace, or the coal-feed in cases where this is continuous, such as rotary cement kilns. On a small scale in the laboratory it is not difficult to arrange a pyrometer to act as a thermostat, and a similar application to large-scale operations may reasonably be expected to follow. If the advance indicated can be successfully made, a great boon will be conferred on all industries in which accurate furnace control is of importance.

In concluding a paper of this description, it is necessary to pay a tribute to the National Physical Laboratory for the part it has played in maintaining a high standard of accuracy in connection with all appliances for measuring high temperatures. The value of this institution is appreciated both by makers and users; and to its work and influence may be traced the confidence now felt in the reliability of the instruments described.

DISCUSSION.

The Chairman, in opening the Discussion, remarked that they had at University College the original Siemens pyrometer, which, of course, was not a recording pyrometer, and he contrasted the beautiful instruments on the table with that historic apparatus. Recognizing the great advances that had been made, he did not think that the author was taking any very great risk in predicting further great advances in the future.

Dr. J. A. Harker expressed his indebtedness to Mr. Darling for his very practical paper, which was all the more valuable, as so very little had been written on the subject, and also for the very interesting collection of samples which they were privileged to see. Mr. Darling had made an historical reference to the work of Chatelier. This reminded him that it was at the Sèvres pocelain factory that his first work on pyrometers was carried out, and it was the late Dr. Vogt who succeeded Regnault as the scientific head of the factory who had instigated Chatelier to prosecute his researches.

He had had some experience with the type of Callendar recorder shown that evening by the Cambridge Scientific Instrument Company, and he had found it most useful for scientific experiments, even without the motor drive. With regard to the Paul instrument, it was a great advantage that it was built up from separate interchangeable units. He hoped that some information would be forthcoming from the makers of the various types with regard to the comparative life and efficacy of the different recorders; how often they came back to the makers for repair, etc. He wished to compliment the makers of the beautiful instruments which they were exhibiting, which were a credit to them, and which would hold their own all over the world.

Mr. R. S. Whipple, speaking as a manufacturer, thanked Mr. Darling for his impartial treatment of the subject. As a matter of historical interest it should be mentioned that the first mechanical recorder used with thermo-electric pyrometers was that developed by Mr. William Bristol, of the Bristol Recorder Company. In this instrument a smoked chart is rotated by clock-work, and the galvanometer needle makes a record on the sheet by moving particles of soot from the smoked surface.

The Callendar Electric Recorder was introduced in 1898 and not in 1899 as stated in the paper. He thought that the difficulty of working this instrument was over-rated. Over four hundred of these instruments were in use, and the majority of them were in charge of men not specially skilled in the care of instruments.

The great advantage of the resistance type of pyrometer was the fact that it either was working or out of action, and in this way it had a great advantage over the thermo-electric type of pyrometer, in that the latter might apparently be recording correctly although it was recording inaccurately. It was impossible for this to occur with the resistance pyrometer; it was either recording correctly or failed to record entirely.

The paper suggested that very little had been done in the way of controlling temperature automatically, but he thought that this was hardly the case. He knew of an ironworks in Wales where the temperature of the air in the hot main leading into the furnaces was controlled automatically by means of a pyrometer inserted in the main, the temperature of the air being maintained constant within $\pm 10°$ C. at 700° C.

Another practical instance of temperature control that he knew of was the control of the temperature of a large soldering-iron used in soldering tin cans in a large preserve factory. In this case the temperature of the iron was maintained constant within 2 or 3° C.

Another very useful example of temperature control was that of the spectroscope used on the McLean telescope at the Cape of Good Hope Observatory. This instrument was used for determining the velocity of stars in the line of sight, and this work demanded that the spectroscope should be kept at a constant temperature. A special electrical thermostat was designed for use with a resistance thermometer mounted in the spectroscope casing, and the temperature of the instrument was maintained constant by means of electric heating to with 1/100° C., although the temperature of the air surrounding the telescope might alter as much as 30° C. during twenty-four hours.

Mr. Lamplough, working in the Chemical Laboratory at Cambridge, had also designed a simple attachment to the Callendar Recorder, which enabled him to maintain the temperature of an electric furnace constant to within 2 or 3° C. at temperatures as high as 800° C.

Speaking generally, he was certain that the secret of all thermometric control was to interest the firemen or other employees who were controlling

the sources of heat in the behaviour of the instruments. If they are convinced that the pyrometers are put in to help them to turn out better work and not simply as policemen to see that they are fulfilling their obligations, then they become interested in the instruments, and begin to rely upon them. For this reason the instruments should be fitted up alongside the furnaces so that the firemen can see them without difficulty, instead of in the Office, where they are only seen by the Works Manager or some other highly-placed official.

Mr. C. E. Foster also complimented Mr. Darling on the practical nature of his paper. He thought that automatic control was always possible if it was wanted ; it was really the users who needed educating.

He emphasised what the author had said with regard to dust being a great enemy of the recording instrument, and he could bear this out from his own experience on Cement Works. He anticipated a much extended use of thermo-couples made of base metal alloys, as these gave comparatively large e.m.fs. which remained constant, and thus allowed the use of a robust recording instrument.

Mr. E. H. Rayner suggested that it would be of great value if Dr. Harker could supply a list of the most useful standard temperature melting and boiling points, with a few notes as to any precautions which ought to be observed in using the various substances.

Mr. Robt. W. Paul disclaimed any originality for the use of a motor for recorder driving ; a motor with a governor for regulating its speed to one part in ten thousand had been constructed many years ago by the Reichsanstalt.

He had constructed a governor upon the same principle, but he had found it inconvenient for regulating while in action, and had therefore developed another form of governor which would hold the speed constant on any circuit, even if the voltage variation were 15 or 20 per cent. The timing adjustment was accessible to the user without opening the case or stopping the motor.

The ample power provided by the motor rendered it easy to apply a simple switching device to give almost any number of records on one chart. As an example he mentioned an instance where the temperature of a large number of vats had to be controlled. Resistance thermometers were used in conjunction with a recorder embodying the Harris resistance indicator principle. By suitably graduating the chart and fitting the recorder with a change-over switch, the temperature and number of each vat are recorded in different colours, the vat numbers being read off from the temperature ordinates. In this instance it was desirable to insure that the attendant should inspect each tank at stated intervals ; to check this a switch was placed near each tank, and the operator closed each switch to start the record.

The problems involved in producing a satisfactory recorder were many and fascinating, and it is no easy matter to produce an instrument dealing with the small forces involved, and, at the same time, one robust and capable of continuous work under workshop conditions.

Mr. Darling, in reply, said that he had hoped for stronger criticisms of some of the points raised by the Paper. He quite agreed with Dr. Harker's remark concerning the dearth of literature on the subject, and stated that most of the useful research on the production of recorders had, in recent years, been confined to the instrument makers. He was of opinion that the subject of pyrometry did not receive the attention it deserved in our colleges and technical institutions. Referring to Mr. Whipple's remarks on Callendar

recorders, he expressed the opinion that this instrument should only be used under skilled supervision, and in places free from vibrations, as it was somewhat delicate in construction. The question of the relative advantages of thermoelectric and resistance pyrometers opened up a large problem; his own preference was for the former type, particularly for the purpose of an installation. In this connection he might mention the procedure adopted by Colonel Holden, F.R.S., in the Royal Arsenal at Woolwich, for working a large number of pyrometers in unison. Special ingots of platinum and iridio-platinum were cast and drawn into wires, so that a large number of couples could be made of identical thermoelectric value. All the indicators were marked, and the recorder charts prepared, by comparison with a standard instrument in charge of the metallurgist, thus securing complete agreement. The successful results which had accrued in the heat treatment of steel had amply demonstrated the value of such an installation.

The extension of the use of base-metal couples, referred to by Mr. Foster, was the natural sequel to the high price of the platinum metals. Now that satisfactory base-metal couples were procurable, some of which could be used up to 1,200° C., he was of opinion that platinum and its alloys would largely be superseded, as even these metals gave trouble, under workshop conditions, above 1,200° C. For temperatures higher than this a radiation pyrometer was far more suitable.

In reference to the subject of furnace control, which had been touched upon by several of the speakers, he had in mind the automatic adjustment of the fuel supply or current in the case of large furnaces, which, so far as he was aware, had not yet been attempted. Small furnaces could easily be controlled by a mechanism connected to a recorder; but when it came to a question of working large valves it was obvious that considerable power would be necessary, and motor-driven recorders appeared to him the most promising type for the successful solution of this problem. In conclusion, he expressed his thanks to the various makers who had so kindly exhibited their apparatus.

THE ACIDIC AND COLLOIDAL PROPERTIES OF ALUMINIUM HYDROXIDE.

By R. E. SLADE, D.Sc., and W. G. POLACK, B.Sc.

(*A Paper read before the Faraday Society, Wednesday, April 22, 1914,* Professor Alfred W. Porter, F.R.S., *in the Chair.*)

In a recent paper by Mahin, Ingraham, and Stewart* it is claimed that there is no evidence of the amphoteric nature of aluminium hydroxide. These authors consider that the so-called sodium aluminate solutions are really colloidal solutions of aluminium hydroxide in sodium hydrate solution. They do not appear to have seen the work of Wood,† of Slade,‡ of Klein,§ or of Hantzsch.‖

In the above-mentioned paper the conclusions which the authors draw from their experiments and from those of former investigators are open to very serious objections, and in one case exception must also be taken to their experimental method.

Their assumption that aluminium hydroxide cannot be amphoteric because aluminium has a high heat of oxidation and because it stands in the potential series near to the alkaline earths is an hypothesis which is not supported by experience.

Noyes and Whitney ¶ found that there was no change in the freezing-point of a caustic soda solution on dissolving aluminium hydroxide in it. They explained this by supposing aluminium hydroxide to act as a monobasic acid; the reaction being

$$Al(OH)_3 + OH' \longrightarrow Al(OH)_2O' + H_2O,$$

which causes no change in the total ion concentration. Mahin, Ingraham, and Stewart now tell us that this explanation is wrong. They say that hydrolysis must take place and "by the hydrolysis of one molecule of $NaAlO_2$ there would be produced three particles which would have an influence on the freezing-point of the solution; two ions from the NaOH of hydrolysis and one molecule of aluminic acid." They forget that aluminic acid is practically insoluble in water.

These authors have attempted to determine the heat of solution of aluminium hydroxide in a base. They did one experiment, using 7·452 normal sodium hydroxide as the base, and they seem to have expected to get the heat of neutralization of a dilute acid with a dilute base if aluminium hydroxide was at all acidic, thus completely overlooking the heat of solution and of dissociation of the aluminium hydroxide, the heat of dissociation of the sodium hydroxide, and the heat of combination of the ions of sodium

* *Journ. Amer. Chem. Soc.*, xxxv., 30.
† *Journ. Chem. Soc.*, xciii., 421 (1908).
‡ *Zeit. für Elektrochemie*, xvii., 261 (1911); *Ibid.*, xviii., 1 (1912); *Zeit. für anorg. Chem.*, lxxv., 457 (1912).
§ *Ibid.*, lxxiv., 157 (1912).
‖ *Ibid.*, lxxv., 371 (1912); *Ibid.*, xxx., 289
¶ *Zeit. für phys. Chem.*, xv., 694 (1894).

aluminate, for the latter would be little dissociated in so strong a sodium hydroxide solution. They do not appear to have protected this strong sodium hydroxide solution from carbon dioxide in the air : this may account for the steady rise of temperature of the solution before mixing. Their method of interpreting their temperature readings is also open to objection.*

These authors next show that the amount of aluminium hydroxide precipitated by ammonium nitrate is not exactly according to the equations

$$NH_4NO_3 + NaAlO_2 = NH_4AlO_2 + NaNO_3$$
$$NH_4AlO_2 + 2H_2O = NH_4OH + Al(OH)_3.$$

But this is not what would be expected, for Slade † has shown that there is an equilibrium in these solutions between the amounts of hydroxyl and aluminate ions. If ammonium nitrate is added the hydroxyl concentration is lowered, the equilibrium is disturbed, and aluminium hydroxide is deposited, but not an amount exactly equivalent to that of the ammonium nitrate added. The quantity deposited will depend upon the temperature and the absolute concentration. Similar objections apply to the electrolysis experiments : At the anode, hydroxyl or aluminate ions are discharged, the equilibrium is disturbed and aluminium hydroxide is deposited. The actual amount deposited depends upon the temperature, the concentration, the current density and the efficiency of stirring in the anode compartment.

The work of Hantzsch ‡ on the conductivity of sodium aluminate solutions proves that aluminium hydroxide does behave as a monobasic acid. The hydrolysis of the aluminate, which takes place according to the equation

$$Al(OH)_2O' + H_2O \rightleftarrows Al(OH)_2OH + OH',$$

was indicated by the change of conductivity. Hantzsch found, however, that no visible deposition of $Al(OH)_3$ took place until the conductivity had increased very considerably. He believed this to indicate that the $Al(OH)_3$ first went into the colloidal state.

In order to investigate this point the authors have carried out a series of experiments in which the conductivities of sodium aluminate solutions were determined over the period during which hydrolysis took place at an appreciable rate, whilst the solutions were examined from time to time in the ultra-microscope.

The sodium aluminate solutions were prepared in the following way : A solution of sodium hydroxide was prepared by the action of metallic sodium (Kahlbaum's) on conductivity water. The reaction was carried out in a silver bottle in a stream of hydrogen. To the solution thus obtained excess of aluminium § turnings was then added, and the silver bottle connected to a delivery tube leading to a vessel for measuring the volume of hydrogen evolved. During the solution of the aluminium the reaction vessel was cooled by a stream of cold water. The aluminium was allowed to react until the volume of hydrogen collected indicated that the atomic ratio of Al : Na in the solution was nearly 1 : 1. The sodium aluminate solution was then poured off the aluminium into a Jena glass flask immersed in the thermostat, and into the conductivity cell. Measured samples were then taken for analysis before any deposition of $Al(OH)_3$ could take place.

* W. Blum., *Journ. Amer. Chem. Soc.*, xxxv., 1409 (1913), has criticized the work of Mahin, Ingraham, and Stewart, and has given another proof of the existence of aluminates in solution.

† *Loc. cit.* ‡ *Loc. cit.*

§ The aluminium, which was 99·6 per cent. pure, was kindly presented to the authors by Dr. G. H. Bailey, of the British Aluminium Company, Ltd.

The conductivities were measured by the method of Kohlrausch and Holborn. The cells were of dimensions suitable for the concentrations of the solutions being investigated, and were closed either with a ground glass stopper or made air-tight to prevent CO_2 from contaminating the solutions. The electrodes were of platinized platinum.

The ultra-microscope was made by Zeiss. It was fitted with a cardioid condenser.

Conductivity Experiments.

The results of a typical conductivity experiment are shown in Fig. 1.

The aluminate solution was 0·1383 N with respect to sodium and the ratio Na : Al in the solution 1 : 0·95. The temperature of the thermostat was 16° C.

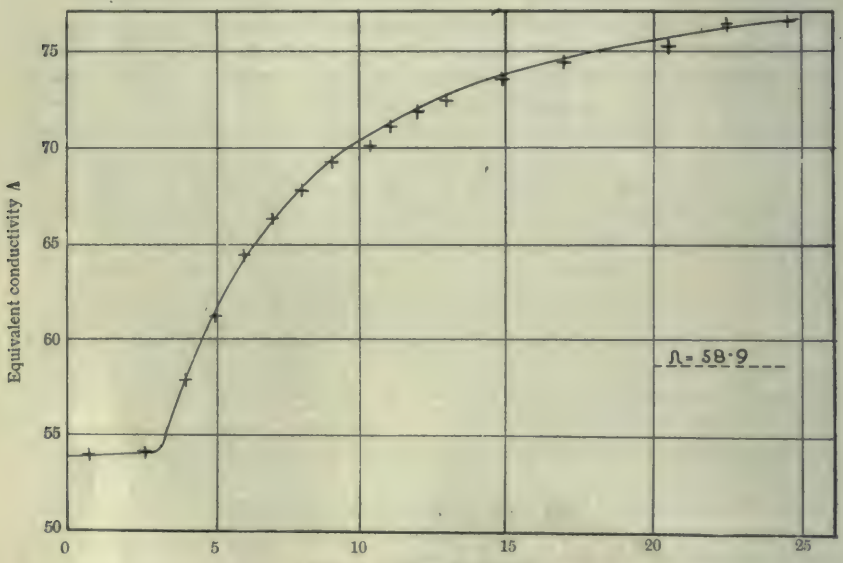

FIG. 1.—Time in Hours.

For the first three and a half hours there was very little change in the conductivity of the solution; then the conductivity increased, at first rapidly and then more slowly. The reaction which takes place is

$$Al(OH)_2O' + H_2O \longrightarrow Al(OH)_3 + OH'.$$

The conductivity of the hydroxyl ion is greater than that of the aluminate ion, so this change is accompanied by an increase in the conductivity. The equivalent conductivity Λ for N/8 NaOH at 16° is 188, and this is the value we should get if the hydrolysis was complete. From the values of Λ for fresh solutions and from the analyses we were able to calculate that the partial conductivity of the aluminate ion was about 18 at this temperature 16° and in N/8 solutions.

If hydrolysis takes place with the formation of colloidal aluminium hydroxide, we should expect the conductivity to rise from the first, but if hydrolysis only takes place on the crystallization of $Al(OH)_3$ we should expect no change until nuclei for crystallization had been formed. The

curve shows that the second alternative is the one that takes place. In all experiments it was found that aluminium hydroxide was deposited in a thin film on the platinized platinum electrodes. In the above experiment, after four hours, a faint grey streak was noticed on one of the electrodes; this gradually spread until at the eighth hour both electrodes appeared to be covered by a faint uniform grey film which might almost have escaped notice had it not been observed during its formation. About the ninth hour the sound minimum in the telephone became less sharp and gradually grew worse until finally there was a considerable range of the bridge over which the sound was a minimum, whereas at the beginning there had been a definite point of absolute silence. In order to determine whether this very marked change was really due to a deposit on the electrodes, these were washed with water and placed in a solution of ammonium chloride of the same conductivity as the aluminate solution: The sound minimum was found to be quite as bad. The electrodes were then placed for a few minutes in a warm strong sodium hydroxide solution, rinsed with water and put back into the ammonium chloride solution. The sound minimum in the telephone was now found to be quite sharp again. It therefore appears that the bad minimum was caused by a deposit of aluminium hydroxide on the electrodes. From the volume of the solution in the cell, its concentration, and the amount of hydrolysis calculated from the increase of conductivity, it was calculated that the quantity of aluminium hydroxide deposited on the electrodes would be about one milligram per square centimetre of electrode surface.

Some of the original aluminate solution which had been standing in a Jena glass flask in the thermostat for forty-six hours was put into the cell and found to have an equivalent conductivity of 58·9, whilst the solution which had been standing in the cell had an equivalent conductivity of 76·8 after twenty-four hours. Apparently the aluminium hydroxide crystallizes more readily on the electrode than on the glass, hence hydrolysis is more rapid in the cell. The solution in the Jena flask had deposited a little aluminium hydroxide on the walls of the vessel at the time when the conductivity was determined.

Experiments were carried out at 14°, 16°, 18°, and 25° with solutions varying from 0·03 to 0·125 N, and in all cases it appeared that no appreciable hydrolysis of the sodium aluminate took place without the deposition of aluminium hydroxide.

Ultra-microscopic Investigation.

In no case were we able to detect the existence of colloidal aluminium hydroxide in sodium aluminate solutions by means of the ultra-microscope. The number of submicrons * present was always comparable with the number present in the sodium hydroxide solutions from which the aluminate solutions were prepared. This is not, however, a definite proof that such solutions are not colloidal, as is shown by the following observations. Some colloidal aluminium hydroxide solutions were prepared by the method of Crum † (hydrolysis of aluminium acetate solution), and were examined in the ultra-microscope for comparison with the sodium aluminate solutions. In the sodium aluminate solutions from 0·01 to 0·125 N there were 0·1 to 1·0 particles visible in a volume which was about $4{\cdot}5 \times 10^{-7}$ cub. mm. In a colloidal $Al(OH)_3$ solution 0·03 Molar there were about 2·6 particles visible

* Submicrons are particles visible in the ultra-microscope. Amicrons are particles too small to be visible.

† *Pogg. Ann.*, lxxxix., 156 (1854).

in this same volume, whilst after gelatinizing this solution by the addition of a trace of sulphuric acid there were from forty to sixty particles visible. The gelatinization was carried out in the cell in which the observations were made with the ultra-microscope, by placing a small drop of dilute sulphuric acid near a drop of the colloidal solution on the slide and then dropping on the cover glass. After two days the sulphuric acid had diffused into the colloidal solution and gelatinized it. This method was adopted in order to show that the large number of particles present was not caused by the cover glass dropping on to a piece of jelly and squashing it out flat. These experiments show that in the colloidal aluminium hydroxide solutions of Crum only about one-tenth to one-thirtieth of the colloid is visible in the ultra-microscope. It is probable that if the colloidal solution was made in some other way the ratio of the number of submicrons to the number of amicrons would be different. From the observations with the ultra-microscope we are unable to draw any definite conclusion as to the existence or non-existence of colloidal aluminium hydroxide in sodium aluminate solutions. For though so few particles were seen it would be possible for the colloidal aluminium hydroxide to be present as amicrons.

Summary.

1. The conclusions of Mahin, Ingraham, and Stewart that aluminium hydroxide has no acidic properties are criticized.

2. Experiments on the conductivity of sodium aluminate solutions show that there is no evidence of the existence of colloidal aluminium hydroxide in these solutions, as was supposed by Hantzsch. Whenever hydrolysis takes place crystalline aluminium hydroxide is deposited.

3. An examination of sodium aluminate solutions in the ultra-microscope gave no definite evidence as to the existence or non-existence of colloidal particles. In the colloidal aluminium hydroxide solutions of Crum it was found that the number of amicrons present was very much greater than the number of submicrons.

The ultra-microscope used in this investigation was the property of the Government Grant Committee of the Royal Society. It was kindly lent to us by Prof. F. G. Donnan, F.R.S., to whom we wish to express our thanks.

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ON "NEGATIVE" ADSORPTION.

By A. M. WILLIAMS, M.A., B.Sc., 1851 Exhibition Scholar of the University of Edinburgh.

(From the Muspratt Laboratory of Physical and Electro-Chemistry, University of Liverpool.)

(*A Paper read before the Faraday Society, Wednesday, April 22, 1914,* PROFESSOR ALFRED W. PORTER, F.R.S., *in the Chair.*)

INTRODUCTION.

In 1898 * Lagergren † observed that on shaking up solutions of electrolytes with charcoal or silica the concentration of the salt in the solution *increased* instead of decreasing. This "negative" adsorption fitted in very well with the deductions from Gibbs's ‡ well-known formula. Hägglund § repeated Lagergren's experiments with "pure" charcoal and failed to obtain anything save indications of slight positive adsorption. Lachs and Michaelis ‖ also cite experiments interpreted as contradicting Lagergren's results. Evans ¶ using filter paper as adsorbent, found an adsorption maximum passing to zero, but not negative adsorption. More recently numerous examples of "anomalous" adsorption ** have appeared, where the adsorption passes through a maximum and decreases instead of continuously increasing with increase of concentration, while Schmidt †† believed he had observed a maximum of adsorption with acetic acid solutions, but this appears to the author to be erroneous.‡‡ In studying adsorption by crystals, Marc §§ also appeared to find a maximum, but his interpretation of it differed from Schmidt's.

Several experimenters ‖‖ have obtained maxima and minima of adsorption and also negative adsorption working with more than one substance in solution. But, in such cases, the possibilities of chemical action are not excluded (and the method of calculation is open to the same criticism as is directed against Schmidt).

* After this was written I found a paper by Gore, *Chem. News* (1894), 69, pp. 23, 33, 44, containing numerous cases of negative adsorption by silica. Trouton, B.A. Report, 1911, p. 328, seems to have repeated some of Gore's work.

† *Bihang till K. Svenska Vet.-Akad. Handlingar*, 24, ii., 4.

‡ Works, I, p. 336. See also J. J. Thomson, *App. of Dyn. to Phys. and Chem.*, p. 191.

§ *Koll. Zeitsch.*, 7, p. 21.

‖ *Zeitsch. f. Elektroch.*, 1911, p. 1.

¶ *Journ. Phys. Chem.*, 10, p. 290.

** Biltz u. Steiner, *Koll. Zeitschr.*, 7, p. 112. Herzog u. Adler, *Koll. Zeitschr.*, 1, Suppl. Heft 2. Michaelis u. Rona, *Bio. Zeitschr.*, 15, p. 196, etc. Freundlich, *Zeitsch. f. physik. Ch.*, 73, 385. Dreyer and Douglas, *Proc. Roy. Soc.*, 82 (B), p. 185. Morawitz, *Koll. Beihefte*, 1, p. 301. Lottermoser, *Zeitsch. f. physik. Ch.*, 62, p. 377. Moore and Ryland, *Bio. Journ.*, 5, p. 32, etc.

†† *Zeitsch. f. physik. Ch.*, 74, p. 689 ; 77, p. 641 ; 78, p. 667 ; 83, p. 674.

‡‡ Williams, *Medd. fran K. Vet.-Akad., Nobelinstitut*, 2, 27.

§§ *Zeitsch. f. physik. Ch.*, 76, p. 58.

‖‖ Estrup, *Koll. Zeitsch.*, 7, 299 ; *Oversikt, K. Danske Vid-Sels. Förh.*, 1912, No. 4 ; 1913, No. 1. Oryng, *Koll. Zeitsch.*, 13, pp. 9, 14, etc.

If M grams of solution of, say, a salt in water be shaken up with G grams adsorbent, and if the concentration of the salt be c_o grams per gram solution initially and c finally, then the amount adsorbed in grams per gram adsorbent (if no water is adsorbed) is

$$u_o = \frac{M}{G} \cdot \frac{c - c}{1 - c}.$$

But if w grams water per gram adsorbent be adsorbed then the amount should be

$$u = u_o + w \,.\, c/1 - c.$$

(Also, if the area of one gram adsorbent be A then we may put in Gibbs's equation:

$$\frac{u_o}{A} = \Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}\Big)$$

It has been generally found that if c is small, u_o is positive.* As long as no chemical action takes place and the relative adsorption of the two substances, salt and water, appears to depend on their relative masses present, it seems natural to assume that with c nearly equal to unity more water than salt will be adsorbed. Hence we may expect that u_o will at first increase to a positive maximum, decrease, pass through zero and become negative (probably being equal to $-\infty$ when $c = 1$). This would explain and reconcile the results of Lagergren, Evans, Lachs and Michaelis, etc.

Experimental Part.

Blood charcoal from Merck was being purified by washing for certain experimental purposes and the opportunity of testing the above idea suggested itself. The charcoal was cleaned by boiling up with distilled water, and finally by repeated washings in the cold. The conductivity of the washings fell from 120×10^{-6} mhos to $4 - 5 \times 10^{-6}$ mhos at 25° C.,† where it remained steady. The conductivity of the water employed was 2×10^{-6} mhos. This final preparation was used with solutions of several electrolytes. The changes of concentration in the solutions, after treatment with the charcoal, were found to be small. In general about five grams of charcoal were shaken up with 100 grams solution in a Jena flask closed with a paraffined cork. Along with every experiment a blank was performed, a hundred grams of solution being shaken up without charcoal. The flasks were rotated for 24 to 48 hours in a thermostat at 25° C. The concentration of the solutions was determined as follows: Similar amounts were withdrawn from the original solution, the blank and the test solution (free from charcoal of course). They were then diluted down to the same extent. All dilutions were done by weighing. The concentrations of the resulting solutions were then determined from their conductivities, employing the telephone method. No change was observed between the blank and the original solution.

Alternate readings were then taken with the diluted blank and test solutions. Thus first the diluted blank solution, then the diluted test solution, then again the former, then again the latter were placed in rotation in the same conductivity cell (washing out, of course, with the replacing solution each time), with the same resistance out in the box and hence reading near the same place on the bridge. When the two pairs of readings were found concordant, they were accepted. The ratio c_o/c was

* See, however, Gore, *loc. cit.*, Trouton, *loc. cit.* Instances are given of negative adsorption at low concentrations becoming positive adsorption at higher concentrations.

† Allowing 10 grams water to 1 gram charcoal.

thus determined with as great accuracy as the method and the apparatus employed allowed. The readings on an ordinary metre bridge were taken to the nearest tenth of a millimetre. Assuming an error of ·1 mm. in opposite directions in the two readings, the error in c_o/c would be 8 in 10,000.

It is possible that, since Kohlrausch and Holborn's tables were used for interpolation to determine the concentration in the diluted solutions, the values of c_o and c may be out in the same ratio by a small percentage. But this is unimportant, and c_o/c is unaffected. A sharp minimum was always obtained by diluting sufficiently—generally 25 c.c. were made up to 2 litres with the more concentrated solutions. The error introduced into calculation by error in dilution would be less than 1 in 10,000. The solutions were also tested with methyl orange, phenolphthalein, and in some cases rosolic acid, but no change in their behaviour to these reagents occurred after being shaken up with charcoal. The salts employed were the purest preparations.

The observations are as follows :

KCl.

c.	c_o/c.	u_o.
·00044	1·027	+ ·00032
·00266	1·021	+ ·00128
·00616	1·018	+ ·00230
·0205	1·0061	+ ·0025
·0398	1·0014	+ ·0011
·0563	1·0014	+ ·0017
·0680	0·9988	− ·0017
·0721	·9990	− ·0018
·101	·9995	− ·0012
·128	·9990	− ·0026
·170	·9981	− ·0077

NH_4Cl.

·0122	1·0060	+ ·0015
·0229	1·0077	+ ·0034
·0489	1·0114	+ ·0119
·0992	1·0035	+ ·0074
·152	1·0013	+ ·0045
·191	1·0007	+ ·0033

$BaCl_2$.

·095	1·0123	+ ·026
·153	1·0070	+ ·028
·220	1·0055	+ ·036

$CuSO_4$.

·067	1·020	+ ·033
·114	1·007	+ ·024

$MgSO_4$.

·00043	1·101	+ ·00089
·00123	1·072	+ ·0024
·0257	0·991	− ·0044
·0516	·987	− ·014
·0528	·986	− ·016
·1001	·986	− ·034
·1538	·990	− ·039

It will be seen that with KCl and $MgSO_4$ maxima of u_o were found, and u_o afterwards became negative ; with NH_4Cl a maximum was found, but at great concentrations negative adsorption had not yet been found. With $BaCl_2$ even at great concentrations the adsorption was still increasing ; and nothing can be said about $CuSO_4$.

SUMMARY.

It has been experimentally found with some electrolytes in water that the "adsorption" is at first positive, increases to a maximum, decreases, passes through zero, and becomes negative.

Attention is therefore drawn to the fact that with different concentrations of the same solution both positive and negative "adsorption" of the solute may be observed. Hence both solvent and solute must be regarded as being adsorbed.

These experiments were performed in May and June in the Muspratt Laboratory. To Professor F. G. Donnan, F.R.S., are due the thanks of the author for interest, encouragement, and advice.

DISCUSSION.

The Chairman remarked that though the recognition of the simultaneous adsorption of water and salt served to clear up much of the behaviour in cases of anomalous adsorption, he was very doubtful whether it was competent to explain everything. For example, it threw no light on the experimental results obtained by Professor Trouton and referred to in the paper. He added, further, that the correction to be made for the water adsorption depended upon the relative quantities of solution and adsorbent taken ; and in most of Professor Trouton's work the amount of solution taken was so large that the correction necessary could only be very small. This was fortunate, because it was very difficult to estimate the amount of water adsorbed.

Mr. A. M. Williams : The correction on u_o for water adsorption for any given equilibrium concentration depends solely on that concentration, and hence is *independent* of the volume of solution relative to one gram adsorbent. For suppose a gram of adsorbent is in equilibrium with a solution containing equal masses of solvent and solute. Then, if the adsorbent has taken up one gram solvent, the correction on u_o is one gram also, whether there be 50 or 500 c.cms. of solution. As written above, the correction is $wc/1 - c$, and w is evidently a function of c only. If, however, the calculation has been based on the volume concentrations, the correction is somewhat different, but still approximately independent of the volume of solution taken. For if we denote by u_v the adsorption reckoned on the assumption that the initial volume of the solution v_o does not change and v be the final volume, we have, using a notation similar to above—

$$u_v = v_o(c_o - c).$$

But—

$$u = v_o c_o - vc = v_o(c_o - c) + (v_o - v)c.$$
$$= u_v + (v_o - v)c.$$

Let the specific volumes in solution of concentration c be s_1 and s_2 for solute and solvent respectively. Then—

$$v_o - v = us_1 + ws_2$$

Hence the correction on u_v is $(us_1 + ws_2)c$, which is independent of v_0 and dependent on c only, s_1 and s_2 being regarded as approximately constant near c. The correction *cannot* therefore be altered in *magnitude* for any equilibrium concentration c by varying the *volume* of solution in contact with one gram adsorbent. (It is assumed, of course, that the mass of solution is large compared with $u + w$.) It can only be ignored provided $u - u_v/u$ or $(s_1 + s_2w/u)c$ is small relative to unity in the case of volume concentrations, or $u - u_v/u = wc/u(1 - c)$ is small in the case of mass concentrations as employed by the author.

Until a second equation is deduced connecting u, w, and c, we are not entitled to say that the correction is small, unless other considerations indicate this clearly, *e.g.* with dilute aqueous solutions of acetic acid and charcoal it was found (Williams, *loc. cit.*) that $u_0/c^{\frac{1}{2}}$ was nearly constant and w about ·5. Hence the correction being proportional to $c^{\frac{1}{2}}$ could be made very small by decreasing c. (By taking observations on the adsorption from the vapour phase u and w were determined. So far as the author knows, this is the only case in which they have actually been measured.)

It is obvious that if there was a relation of the type $u/w = kc/1 - c$, then provided k is less than unity, we would obtain negative values of u_0, that is, "*negative* adsorption."

It may further be pointed out that since s_1 and s_2 are not certainly constants if c varies much, u_v will vary with v_0, unless v_0 is very great. Professor Trouton has perhaps found this, but no data are given in such of his results as are published.

The author does not put forward any *mechanism* to explain the phenomenon of adsorption, but merely wishes to emphasise the fact that *both* solute *and* solvent are removed from the main body of the solution—that is, both are in some degree adsorbed.

DIFFUSION AND MEMBRANE POTENTIALS.

By E. B. R. PRIDEAUX, M.A., D.Sc.

(*A Paper read before the Faraday Society, Wednesday, April* 22, 1914, Professor Alfred W. Porter, F.R.S., *in the Chair.*)

When two solutions of the same salt of different concentrations, or of different salts, are separated by a porous diaphragm, there is generally an e.m.f. set up at this which differs in magnitude from the diffusion e.m.f. at the junction of the same two solutions without any separate membrane.

In considering the possible cause of this potential, it would seem to be important to emphasize the distinction between those membranes which are capable of furnishing ions of the electrolyte and those which are not.

There is an essential difference between chemical precipitation membranes, such as those of copper ferrocyanide, and organic tissue membranes, such as parchment, collodion, or gelatine. The former kind may, as Beutner has pointed out, act to some extent like the AgCl and other electrolytically conducting solids investigated by Haber and Beutner; they form a reserve of ions and behave to some extent like metallic electrodes. Beutner, for example, observed an e.m.f. of 0·115 volts which remained steady for ten minutes in the combination:

$$K_4Fe(CN)_6 \mid Cu_2Fe(CN)_6 \mid CuSO_4.$$

He supposes that this e.m.f. is due to the concentration fall between $K^{\cdot}$ in the $K_4Fe(CN)_6$ and the small $K^{\cdot}$ present in the $CuSO_4$. There is a small amount of double ferrocyanide of K and Cu in the membrane which is reversible with respect to K ions. If the $CuSO_4$ side is stiffened with gelatine, so as to prevent the diffusion into the body of solution of those K ions which are continually being produced on this side, then the e.m.f. drops to 0·003–0·010 volt.

This valuable hint as to the nature of $Cu_2Fe(CN)_6$ membrane was not available when the author commenced a series of researches which were devised to ascertain to what extent such a membrane hindered the motion of the ions of a salt—sodium benzoate—which as a whole diffuses through with great slowness. Although potentials were obtained with this solution, which, unlike those observed by Beutner, remained constant over long periods and also gave a regular alteration of e.m.f. with concentration gradient, yet the substitution of another membrane sometimes gave results differing from the former by far greater amounts than could be accounted for by experimental error. The anomaly could only be accounted for by the superposition of irreversible effects and effects of reactions with materials of the membrane, upon those due to the selective hindrances of ionic diffusion.

It was decided, therefore, to investigate those simpler cases in which the latter cause alone was likely to be operative.

This simplification is to be expected in the case of cellulose or other organic tissue membranes, which have a particular importance to physiological chemistry on account of their similarity to animal and vegetable membranes.

The e.m.f.'s observed in muscles, nerves, etc., have been assigned by Ostwald* to a selective permeability of ions. The effect may be divided into two parts :

1. Hindrance of ionic motion due to the nature of the solid membrane.

2. Hindrance of ionic motion due to the sugars, starches, etc., which alter the properties of the solution within the membrane as compared with the solution outside.

The following investigation obviously deals with the first of these effects.

The simple theory of an e.m.f. due to selective permeability of two ions through a membrane is of course merely an extension of the theory of diffusion potential. A diffusion e.m.f. is found for the membrane which is supposed to be due to the difference in the relative ionic mobilities in that medium as compared with the ionic mobilities in the solution. Little experimental work appears to have been done with the following definite objects :

1. Ascertaining over what range of concentration, if any, a constant transport number of the anion in a membrane could be defined.

2. How far such transport number differs from that in the solution.

To a research on the diffusion potential due to sharp and mixed surfaces of separation Cumming † has added a note on the use of membranes. The symmetrical combination

$$(1)\ \mathrm{HgHgClN{\cdot}KCl} \underset{a}{|} \text{connecting solution} \underset{b}{|} \mathrm{N{\cdot}KClHgClHg}\ (2)$$

was rendered unsymmetrical by the interposition of a membrane at *a* while at *b* the liquids were mixed. If the membrane was parchment the electrode (1) on the side of the membrane was + to the other to the extent of 3 mv. when the connecting solution was HCl, and (1) was about 6 mv. − to (2) when the connecting solution was NaOH. With LiCl (1) was + to (2) by 0·6 mv.

These results on the whole point to a strengthening of the diffusion potential by the membrane, *i.e.*, to an exaggeration of the differences between the anion and kation mobilities. The difference between membrane and diffusion potentials gradually disappeared with time, indicating perhaps a gradual removal of the mixed layer from the membrane by diffusion.

In the following series of measurements parchment paper was chosen as the membrane material on account of its wide employment in chemical and biological researches, which gives a value to any additional knowledge of its properties.

A salt was required which should, as a whole, diffuse only slowly through the membrane, and which should not furnish any appreciable amount of H′ or OH′ by hydrolysis. Sodium benzoate proved suitable in these respects. It was considered important to use a binary salt in order to reduce the uncertainty in the calculation of ionic concentrations.

The amount of sodium benzoate diffusing from a N/5 solution through parchment into pure water was found to be small. It was not sufficient to

* *Zeits. Physik. Chem.*, **6**, 71, 1890.
† *Trans. Far. Soc.*, 7, 5, 1913.

influence the e.m.f. in a day, if the weaker side was at least N/10. When there was N/2 solution on one side and N/100 upon the other a slow fall of e.m.f. with time was observed. In such cases the more dilute or both solutions were analysed immediately after reading the e.m.f.

The combination actually used was—

$$\mathrm{HgHgClN{\cdot}KCl} \;\Big|\; \underset{C_1}{\mathrm{NaB}} \;\Big|\; \underset{C_2}{\mathrm{NaB}} \;\Big|\; \underset{\text{membrane}}{\mathrm{N{\cdot}KClHgClHg.}}$$

The temperature variation of the membrane e.m.f. itself for variations of a few degrees in the neighbourhood of 18° was shown to be unimportant; that in the calomel electrodes is, of course, eliminated by their opposition. The equality in temperature of the two electrodes was in most cases checked by a measurement of the one against the other when they were connected by N·KCl.

The diffusion potentials of N·KCl against C_6H_5COONa at concentrations C_1 and C_2 was eliminated by a concentrated solution of potassium chloride (3·5 N). At present it cannot be stated certainly that the saturated KCl eliminated the diffusion e.m.f. at the junctions—

$$\mathrm{N{\cdot}KCl} \;\Big|\; \underset{C_1}{\mathrm{C_6H_5COONa}} \qquad \mathrm{N{\cdot}KCl} \;\Big|\; \underset{C_2}{\mathrm{C_6H_5COONa},}$$

but the probability that these were either eliminated or brought to very low values, and their difference therefore almost eliminated, is strengthened by the result of the measurements of the diffusion e.m.f. of C_6H_5COONa C_1 against C_2.

The membrane was secured by rubber rings and metal clamps between two flanged glass tubes held horizontally, closed at the ends by stoppers containing glass tubes bent at right angles to make connection with the calomel electrodes. The e.m.f. became constant as soon as the combination was set up, whereas that of the copper ferrocyanide previously investigated often required half an hour or more to attain a steady value. The more dilute solution was in all cases positive.

Ionic Concentrations.

These were calculated from the molecular conductivities in the usual manner. The data in Kohlrausch and Holborn's *Leitvermogen* were supplemented by determination of conductivities from 0·1 N to 1 N.

The values at 25° are as follows:

$C =$	1·0	0·5	0·2	0·1	0·05	0·02	0·01
$\lambda =$	42·2	52·6	62·0	67·2	70·4	74·5	76·5
						interpolated.	

The values of [Na·] or ac as tabulated below were plotted against C and the values ac in the table have been read off from this.

$C =$	0·01	0·02	0·05	0·10	0·20	0·50	1·00
$ac =$	0·0086	0·0167	0·0395	0·0755	0·139	0·295	0·472

Diffusion Potentials.

The transport numbers of Na· and C_6H_5COO' in aqueous solution with which were to be compared those in the membrane may in the first place be determined from the data collected by Bredig.* From the ionic mobilities

* *Zeits. Physik. Chem.*, **13**, 191 (1894).

at high dilution of $Na^{\cdot} = 49{\cdot}2$ and $C_6H_5COO' = 31{\cdot}2$, the transport number of the anion (n_A) is 0·388 and $1 - 2n_A$ is 0·224. It was desirable to supplement this by a determination of the average transport numbers in more concentrated solutions. This was done by measuring a series of diffusion potentials.

From the equation—

$$\text{Diffusion potential, } E_d = 0{\cdot}058\,(1 - 2n_A) \log \frac{a_1C_1}{a_2C_2}$$

the mean value of $1 - 2n_A$ could thus be determined.

The measurement was carried out in a similar manner to that of the membrane potential, the place of the membrane being taken by a syphon tube containing the more dilute of the C_6H_5COONa solutions. No special care was taken to preserve a sharp boundary between dilute and concentrated solution, since, in the first place, no change of E was observed within a moderate time; such a change would have taken place if the progress of the mixing with time had been capable of producing it. Cumming * also has been unable to detect any potential difference due to the opposition of a completely mixed and a sharp contact between two electrolytes.

The results indicate that the relation between E_d and $\log \frac{a_1C_1}{a_2C_2}$ is nearly linear, and that therefore there is a mean transport number which does not vary much with the dilution.

The e.m.f. between a 0·1 and 0·01 solution is, *e.g.*, almost identical with that between 1·0 and 0·1 solution :

E(mv.) ...	12·8	17·5	21·2	25·1	12·85	22·6
C_1, C_2 ...	0·1, 0·01	0·2, 0·01	0·5, 0·01	1·0, 0·01	1·0, 0·1	1·0, 0·02
$\log a_1C_1 - \log a_2C_2$ ...	0·945	1·20	1·53	1·74	0·79	1·45

These results are shown by the lower line on the graph. The best linear equation connecting E and $\log \frac{a_1C_1}{a_2C_2}$ was calculated by the method of least squares, and it was found that

$$E(mv.) = 1 + 13{\cdot}5 \log \frac{a_2C_1}{a_2C_2}.$$

On the above assumptions the linear graph should pass through the origin; actually it is + 1 millivolt away. The average value of $1 - 2n_A$ is

$$\frac{13{\cdot}5}{58} = 0{\cdot}234$$

and

$$n_A = 0{\cdot}383.$$

The transport number of the anion therefore agrees well with that calculated from the ionic mobilities at infinite dilution, *i.e.*, 0·388.

Membrane Potentials.

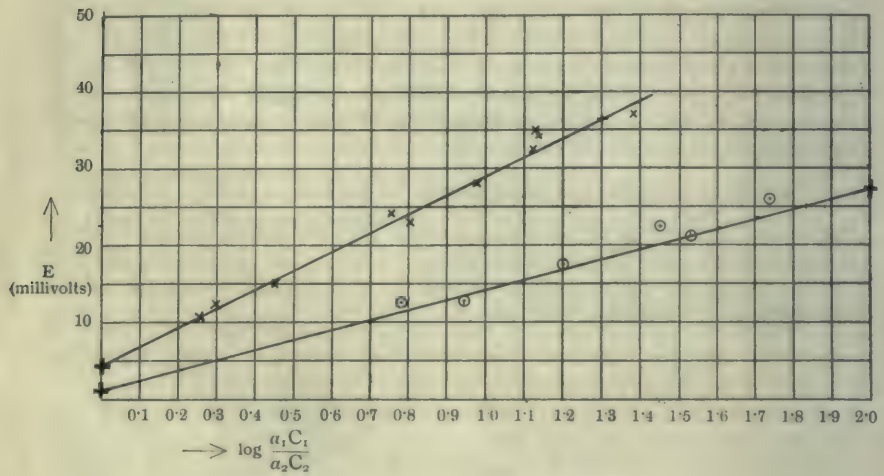
The potentials observed when the diffusing layer is on a parchment membrane are considerably higher than the ordinary diffusion potentials, although they do not in any case reach the value $E(mv.) = 58 \log \frac{C_1}{C_2}$ corresponding to $n_A = 0$, or a membrane impermeable to the benzoic anion.

* *Loc. cit.*

On the above assumptions the effect of the membrane appears to be to decrease the mobility of the anion compared to that of the kation.

The relation of $\log \frac{a_1 C_1}{a_2 C_2}$ to E is here also approximately linear, and from it an average transport number in the membrane has been calculated.

The magnitude of the deviations may be seen on the accompanying graph. They may perhaps be due in part to the uncertainty in the calculation of ionic concentrations from conductivities. The theory has also been somewhat severely tested by the employment of such different ranges of concentration. Thus it has been assumed that a fall of ionic concentration between 0·5 and 0·05 will produce the same e.m.f. as the fall between 0·2 and 0·02.



Electromotive Force and Ionic Concentration.

⊙ ⊙ Diffusion e.m.f.
× × Membrane e.m.f.
+ + Calculated from equation.

In the following table the total concentrations of the two solutions are given in the first column, C_1, C_2. The second column contains the logarithms of the ratios of ionic concentration, the third the observed e.m.f. in millivolts:

C_1, C_2	$\log \frac{a_1 C_1}{a_2 C_2}$	E (millivolts).
0·202—0·1007	0·26	10·80
0·505—0·209	0·30	12·20
0·202—0·064	0·44	14·95
0·202—0·025	0·81	23·05
0·505—0·064	0·76	24·20
0·202—0·0212	0·98	28·25
0·501—0·0252	$1·12_5$	32·60
0·505—0·0245	1·14	34·45
0·202—0·012	1·13	35·10
1·010—0·023	1·39	37·25

The numerical constants of the linear equation

$$E = a + b \log \frac{a_1 C_1}{a_2 C_2}$$

are found to be

$$E(mv.) = 4{\cdot}53 + 24{\cdot}8 \log \frac{a_1 C_1}{a_2 C_2}$$

Hence—

$$58(1 - 2n_A) = 24{\cdot}8$$

and

$$1 - 2n_A = 0{\cdot}428 \quad n_A = 0{\cdot}286.$$

It is remarkable that this graph does not, as in the case of diffusion potentials, pass almost through the origin but intercepts an ordinate of 4·5 millivolts. Pending further investigation the author is unable to suggest an explanation of this. For zero difference of concentration the observed E falls to zero. It may be that the function assumes other forms between the smaller differences of concentration observed (about 2 to 1) and zero difference.

For such differences in concentration as lend themselves to measurement the transport number of the anion is apparently decreased in the ratio $\frac{\cdot 286}{\cdot 388} = \cdot 74$, *i.e.*, the transport number of the anion in the membrane is less than ¾ of that in the free solution.

Further work on similar lines will, it is hoped, decide the applicability of the above hypothesis to other cases, and also whether it is true in general that the mobility of the slower ion is apparently checked by such a diaphragm.

This work was done at the Muspratt Laboratory of the University of Liverpool in 1913.

DISCUSSION.

Dr. R. E. Slade pointed out that there was no very great difference between the membranes used by Bentner and those used by the author. In both cases the thermodynamic method of calculating the e.m.f. is the same. In the theory of these potentials due to Donnan* no assumption is made concerning the mechanism by which the ions move through the membrane.

The Chairman remarked that although no doubt all kinds of membranes must fall within the application of the same general thermodynamical principles, yet in applying these principles to specific cases any differences which may exist in the circumstance must be duly taken into account. He considered that Dr. Prideaux's explanation of his difference in the diffusion and membrane potentials was very plausible. A retardation in the velocity of the slower ion with respect to the other would have the effect obtained. A mechanical explanation of this kind gives in reality more information than can be obtained from thermodynamical principles alone and for that reason is to be preferred. [It should not be forgotten that the usual thermodynamical treatment of diffusion potentials is approximate only. Diffusion is essentially an irreversible phenomenon; and therefore it is incorrect to use principles which are true only for reversible phenomena. It is tacitly assumed, however, that since the phenomenon of diffusion proceeds exceedingly slowly, no much error can be made by treating the system as in quasi-equilibrium.

* *Zeit. für Elektrochem.*, 1911, p. 572.

The assumption is justifiable; though it would be difficult to estimate which magnitude of error it introduces.]

Dr. E. B. R. Prideaux, in reply, said he was in full agreement with Mr. Slade that, given of course the fall in ionic concentration, the thermodynamic calculation was independent of the mechanism assumed. What he wished to emphasize, however, was the probable difference between the mode of ionic transfer in the precipitation membranes used by Beutner and that in the present chemically inert parchment membranes. An extension of the simple thermodynamic treatment of diffusion potential is all that is required at present for the latter case. The theory and calculations given by Donnan apply to cases of a different kind. The point raised by Professor Porter was of special interest to all engaged in this work, and new theories concerning the relation between the molecular and thermodynamic parts of the theory of diffusion potentials would be most welcome.

THE ADSORPTION OF VAPOURS.

By A. M. WILLIAMS, M.A., B.Sc., 1851 Exhibition Scholar of the University of Edinburgh.

(*A Paper communicated to the* TRANSACTIONS *of the Faraday Society, June* 1914.)

An investigation by Professor F. G. Donnan and the author on the thermodynamics of adsorption suggested that instead of using log a and log p as variables in plotting adsorption curves (a is the number of c.cm.'s at N.T.P. adsorbed per gram adsorbent at the pressure p) it might be of interest in the case of gases below their critical point to use log a and log p/P, where P is the saturation vapour pressure of the adsorbed vapour in liquid form. This has been done before by Trouton,* who showed that a does not vary greatly with T if p/P is constant, in the case of water vapour adsorbed by flannel.

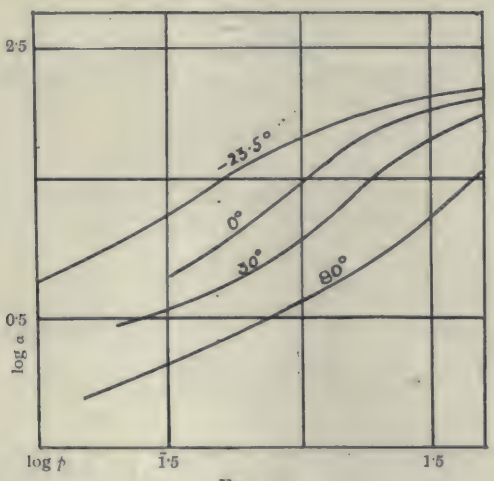


FIG. 1.

The graphs given show the curves for ($\log_{10} a$, $\log_{10} p$) and ($\log_{10} a$, $\log_{10} p/P$) from the observations of Titoff † on the adsorption of ammonia by charcoal. It will be seen that the apparently dissimilar curves of Fig. 1 become more obviously curves of the same type in Fig. 2, and provided there is no sudden change in the curvature near log $p/P = 0$, there is a *finite maximum* of adsorption for $p/P = 1$. Titoff's observations with carbon dioxide may be similarly treated and lead to the same conclusions. Arrhenius ‡ by extra-

* *Proc. Roy. Soc.*, 1905, A, **77**, 292.
† *Zeitsch. f. Physik. Chemie*, 1910, **74**, 641.
‡ *Meddelanden fran K. Veten. Akad.*, Nobel Institut., 1911, **2**, 7.

polating from an empirical formula suggested by the work of Schmidt on solutions deduced a maximum of adsorption which he suggests to be independent of the temperature and supposes to exist even above the critical point.

It can easily be shown from the graphs that $\left(\frac{\Delta \log p/P}{\Delta T}\right)_a$ steadily decreases as p/P approaches unity. This suggests that $\left(\frac{\partial \log p/P}{\partial T}\right)_a = 0$ when $p/P = 1$. Now it may be shown that if a small quantity of gas be adsorbed at *constant* temperature and pressure (not necessarily *equilibrium* pressure) the heat evolved per gram molecule would be—provided the volume of the gaseous phase per gram charcoal is negligible, etc.—

$$\lambda_p = (v - v_0)T\left(\frac{\partial p}{\partial T}\right)_a = RT^2\left(\frac{\partial \log p}{\partial T}\right)_a \text{ approx.}$$

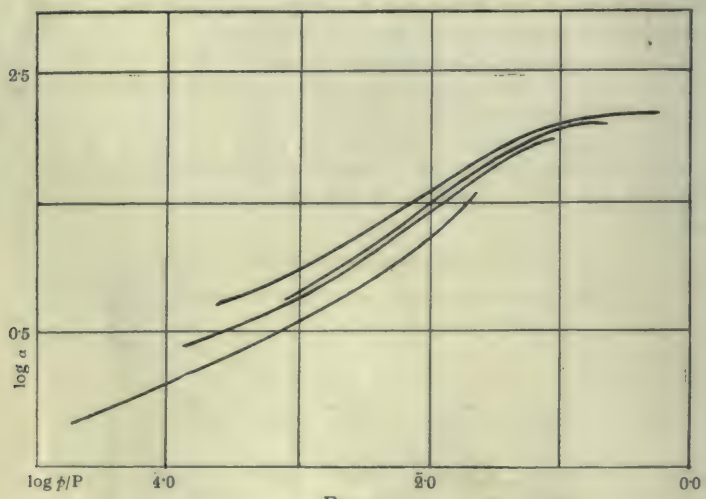


FIG. 2.

The heat of condensation of a gram molecule of vapour at the same temperature is—

$$\lambda_P = (v - v_0)T\frac{dP}{dT} = RT^2\frac{d \log P}{\partial T} \text{ approx.}$$

Here—

v = volume of one gram molecule of gas at p and T.
V = " " " " P and T.
v_0 = " " " of adsorbed gas at p and T.
V_0 = " " " of liquid at P and T.

Hence if *liquid* were adsorbed the corresponding heat would be—

$$\lambda = \lambda_p - \lambda_P = RT^2\left(\frac{\partial \log p/P}{\partial T}\right)_a \text{ approx.,}$$

which is, of course, the well-known formula for the heat of dilution.

Let us consider two curves for $\log p/P$, $\log a$ at temperatures T and $T + \Delta T$ near $p/P = 1$. The difference in abscissæ (Fig. 3) is proportional to λ. It may be expected that this sinks to zero as was previously indicated. Thus

Bellati and Finazzi* experimenting on silica found that the heat of immersion in water sank to zero as the silica was saturated with water vapour. The author found that specimens of charcoal saturated with 70 per cent. benzene and 130 per cent. chloroform by weight respectively evolved no heat on dropping into the corresponding liquids at the same temperature, though ·4 calories per gram charcoal could easily have been detected. (On the other hand air-saturated charcoal evolved per gram more than 25 calories in benzene and 40 calories in chloroform.) Hence, since λ is zero when $p/P = 1$, the difference in abscissæ is zero when $p/P = 1$. That is both the curves cut the line $\log p/P = 0$ at the same place, or *the adsorption when* $p = P$ *is independent of the temperature.*

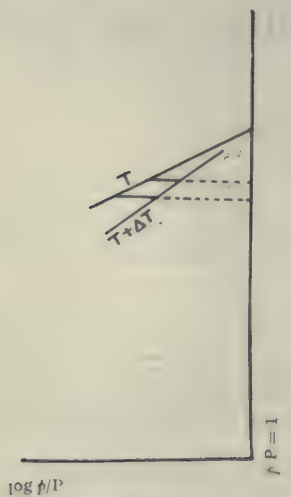


FIG. 3.

Otherwise—

$$\lambda = (v - v_0)T\left(\frac{\partial p}{\partial T}\right)_a - (V - V_0)T\frac{dP}{dT}.$$

Ultimately, when $p = P$,

$v = V$,

$v_0 = V_0$ (very likely),

$\lambda = 0$,

$$\therefore \left(\frac{\partial p}{\partial T}\right)_a = \frac{dP}{dT} \text{ when } \frac{p}{P} = 1 \quad \ldots\ldots\ldots \quad (1)$$

Suppose the relation between a, p, and T can be represented as—

$$a = \phi(p, T),$$

then the value of $\left(\frac{\partial p}{\partial T}\right)_a$ is determined by—

$$0 = \left(\frac{\partial \phi}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_a + \left(\frac{\partial \phi}{\partial T}\right)_p \quad \ldots\ldots\ldots \quad (2)$$

* *Atti del R. Istituto Veneto*, 1900, lix., II., and 1902, lxi., II., p. 507.

The relation between the amount adsorbed for the saturation vapour pressure and the temperature is given by—

$$a_\infty = \phi(P, T),$$

where P is a function of T.

The gradient of this curve, that is, the variation of a_∞ with the temperature, is given by—

$$\frac{da_\infty}{dT} = \frac{\partial\phi(P, T)}{\partial P} \cdot \frac{dP}{dT} + \frac{\partial\phi(P, T)}{\partial T};$$

but, finally, we have from above (1) and (2)—

$$\frac{dP}{dT} = \left(\frac{\partial p}{\partial T}\right)_a = -\frac{\partial\phi(P, T)}{\partial T} \Big/ \frac{\partial\phi(P, T)}{\partial P},$$

when $p = P$.

Hence, since $\frac{dP}{dT}$ is finite, either—

(i) both $\frac{\partial\phi(P, T)}{\partial T}$ and $\frac{\partial\phi(P, T)}{\partial P}$ are infinite, whence a_∞ being equal to $\phi(P, T)$ is infinite identically. This corresponds to the case of solutions which may be diluted to an infinite extent.

or—

(ii) $\frac{da_\infty}{dT} = 0$, or we have a finite saturation pressure adsorption which is independent of the temperature. It should be noted that this is not necessarily a *maximum* in the mathematical sense, so far as we can judge from the thermodynamical investigation above.

It is unfortunate that we are unable to obtain more information concerning a_∞ from $(p/P, a)$ curves. Trouton's results* show a change of curvature comparatively early. This was also found by Masson and Richards† who concluded that a_∞ was infinite. The only other observer who has taken the adsorption up to the vapour pressure (excluding the case of gels) is Hunter‡ who, indeed, gives finite adsorptions at pressures greater than the saturation vapour pressure, *e.g.* his cyanogen figures. His results do not clearly show such a change of curvature. It is uncertain whether they are explicable on the ground that he did not allow the adsorption at the given pressure to be complete when he took readings (the rate of adsorption slows down very considerably near $p/P = 1$ as is easily found experimentally), or whether he obtained supersaturation of the charcoal. Several experiments of the author point to this as a possibility. If charcoal originally *in vacuo* is put into contact with the vapour from the pure liquid in another part of the same vessel and is saturated or nearly so and some of the liquid be dropped upon the charcoal, it has invariably been found that the charcoal + adsorbate loses weight till it approaches "saturation" again. §

These facts support the idea of a finite "saturation pressure" adsorption. The curves from Titoff's observations seem indeed to indicate a *maximum* of adsorption at the saturation pressure of the vapour. But the author has found with sulphur dioxide at $-10°$ C. that when p/P approaches unity, in fact

* *Loc. cit.* † *Proc. Roy. Soc.*, A, **78**, 412.
‡ *Jour. Chem. Soc.*, 1865, p. 285; 1867, p. 160; etc.
§ Compare, however, contra, Masson and Richards, *loc. cit.*

after $p/P = \cdot 9$, the adsorption curve suddenly bends up, as was easily found by Trouton* and Masson and Richards† after $p/P = \cdot 2$ in the case of water vapour. It may therefore be unwise to extrapolate from Titoff's observations.

Summary.

From considerations relating to the heat of adsorption near the saturated vapour pressure of a fluid (the adsorption being reversible) it is deduced thermodynamically that the adsorption is either infinite or finite and independent of the temperature.

Evidence is adduced as to the adsorption being finite, but nevertheless not necessarily a *maximum* in the mathematical sense.

In conclusion the author would seek to express his indebtedness to Professor A. W. Porter, F.R.S., of the Physics Department, University College, for his kindness in reading and assisting him in the presentation of this paper.

University College,
London.

* *Loc. cit.* † *Loc. cit.*

REVIEWS OF BOOKS.

The Viscosity of Liquids. By A. E. DUNSTAN and E. B. THOLE. (London, 1914: Longmans, Green and Co. Pp. 98. Price 3s. net.)

This book forms a volume of the series of monographs on inorganic and physical chemistry edited by Alexander Findlay. It aims purely at giving an account of the relations established so far between viscosity and chemical constitution; as in many similar works on physico-chemical subjects the physics are treated quite inadequately. Thus no definition of the coefficient of viscosity is given anywhere.

An introductory chapter on measurements is practically confined to Poiseuille's formula and the transpiration method. A very full account is given of the work of Thorpe and Rodgers, also of that of Bingham and his collaborators, and the relations between viscosity and "fluidity," *i.e.* reciprocal viscosity established by the latter. Further chapters deal with the viscosity of liquid mixtures, solutions of electrolytes and finally of colloidal solutions. The account of the latter is based on the papers read at the general discussion arranged by this Society in 1913.

The book gives a large number of tabulated results and a good review of the connections so far established between chemical constitution and viscosity. It will be of material assistance to workers in this field, in which a good deal remains to be done, although it is doubtful whether relations between constitution and viscosity will advance our knowledge much until we have gained more insight into the actual mechanism of viscosity than we possess at present.

A Manual of Practical Physical Chemistry. By FRANCIS W. GRAY, M.A., D.Sc. (London, 1914: Macmillan & Co., Ltd. Pp. 211 + xvi. Price 4s. 6d.)

There are now many text-books of Practical Physical Chemistry, most of which are condensed versions of Ostwald-Luther's "Physico-chemische Messungen." A Manual of Practical Physical Chemistry by Dr. Gray is, however, of an entirely different type. The book is primarily intended for a class of three hours' duration, and thirty-nine exercises are given, each of which may be completed within this period. Concise instructions are given for fitting up the apparatus, and indication is given of the method of working out the results, but in most cases the details are not so full that a student may work through the exercise and calculate his results without having to think for himself.

There is an introductory chapter of thirty-five pages on Accuracy, in which a clear account is given of the different methods by which the precision of a series of measurements may be determined. We should, however, like to have seen the principles discussed in this chapter applied more freely to the exercises.

The book is clearly written, well printed, and contains excellent diagrams.

It is certainly well suited for its purpose, a series of three-hour classes. To those also who are able to devote more than three hours consecutively to practical physical chemistry the book should also be useful. For though Honours students at most of our universities now devote a few weeks to laboratory work in physical chemistry, only a few exercises can be done very thoroughly; the rest must be done in as short a time as possible, and for the latter we have seen no better book than this one by Dr. Gray.

Alcoholic Fermentation. By A. HARDEN, Ph.D., D.Sc., F.R.S. Second Edition. Monographs on Biochemistry. (London, 1914: Longmans, Green & Co. Pp. 156, royal 8vo. Price 4s. net.)

Since the first edition of this work appeared in 1909 many investigators have been engaged on this ancient phenomenon, and the importance of their results is shown by the large increase in the subject matter of the book and in the lengthy bibliography. The treatment is the same as before, but a new chapter has been included and deals with the interesting enzyme carboxylase, which is capable of removing carbon dioxide from α-ketonic acids with formation of aldehydes.

It now seems definitely established that methyl glyoxal plays an important part in the formation of alcohol. According to recent work by Neuberg and Kerb this substance, which is derived from sugar via glyceraldehyde or dihydroxyacetone, is converted by a Cannizzaro reaction into glycerol and pyruvic acid. The latter is split up by carboxylase, and the resulting acetaldehyde undergoes another Cannizzaro reaction with more methyl glyoxal forming alcohol and pyruvic acid. The acid reacts again as indicated. This theory explains the presence of glycerol as a by-product.

The function of phosphates in fermentation is fully discussed in the light of the additional observations made during the last few years.

The book is carefully written and gives a most interesting account of the phenomena dealt with, and it should prove invaluable to all students of biochemistry.

Les Courants Vagabonds. By ALBERT PAYOT and ALFRED TOBIANSKY D'ALTOFF. (Paris: H. Dunod et E. Pinat. Price 1 fr. 25, paper covers.)

In this brochure of fifteen pages an account is given of the nature and causes of stray currents occurring mainly in traction schemes with earthed returns. A brief description is given of the electrolytic trouble which these currents cause in piping and cable armouring, and the commoner methods for its reduction are outlined. The latter part of the pamphlet is devoted to a consideration of the inductive disturbances caused in telephone circuits by stray and pulsatory return currents.

The Chemistry of the Radio-Elements. Part II.: The Radio-Elements and the Periodic Law. By F. SODDY, F.R.S. Monographs on Inorganic and Physical Chemistry. (London, 1914: Longmans, Green & Co. Pp. 46. Price 2s. net.)

The appearance of a second part of Prof. Soddy's monograph within three years of the publication of the first part, is an indication of the rapid progress that has been made in radio-chemistry. The present volume has been rendered necessary by two important developments:

(1) The discovery of the law that the expulsion of an α-particle gives a product occupying a position in the periodic chart *two* places earlier than the

original material, whilst the expulsion of a β-particle causes the element to shift *one* place in the opposite direction.

(2) The recognition of "isotopic" elements, *i.e.* elements which differ in atomic weight, but have identical chemical properties and perhaps identical spectra.

In a very brief compass a large number of topics are concisely discussed, no less than twelve chapters being included in the 46 pages of the volume. These include The Periodic Table, and its extension to include the whole of the radio-active elements, The Branching of the Disintegration Series, The Origin of Actinium, Spectra of Isotopes, Neon and Metaneon, Structure of Atoms, and Nature of the Argon Gases. The book will be found to be of great value as a means of securing reliable and up-to-date information on an important and difficult subject.

Photo-Chemistry. By S. E. SHEPPARD, D.Sc. Text-books of Physical Chemistry. (London, 1914: Longmans, Green & Co. Pp. ix + 461. Price 12s. 6d.)

This volume is the twelfth of the series of Text-books issued under the editorship of Sir William Ramsay. It is unfortunate in its Preface, which is both elaborate and obscure in its phraseology. The text is easier to read, but even this might often have been simplified, with great advantage to the comfort of the reader; the descriptive portions are satisfactory, but the author's generalisations are written in a most painful style. Take this as a sample: "The alternative pronouncements in favour of incoherent aether-pulses and a type of corpuscular radiation having up to the present about equal strength, we are left with white light as the sign of, or the actuality of, a transmutation of values which our present symbolic logic seems incompetent to tackle—as though 'das Unbeschreibliche hier wird getan.'"

This description of light is equalled by a description of flames as "very sensitive mobile equilibria of continuously interacting chemical species, in which the act of metathesis is not subordinate to attainment of a static equilibrium, is not monotropic (in essence, exception being made of extrinsic factors which condition practical boundaries or limitations), but is the central and permanent self-reversing condition of their existence"!

Apart from the crude style in which parts of the book are written, the contents will secure for it a welcome from those who are interested in Photo-Chemistry. The subjects dealt with include Radiation and Absorption of Light, the Statics, Kinetics, and Dynamics of Photo-chemical Change, Special Cases of Photo-chemical Effects, Photo-electrical Actions, Photo-synthesis and the Genesis of Light in Chemical Change. In view of the author's special qualifications it is to be regretted that he has dealt so lightly with the photographic plate and the effects of light upon it.

The Simple Carbohydrates and the Glucosides. By E. FRANKLAND ARMSTRONG, D.Sc., Ph.D. (London, 1914: Longmans, Green & Co. Pp. viii + 171. Price 5s. net.)

This book was very favourably reviewed in these columns on its first appearance, and it is satisfactory to find that a second edition has been called for so soon. The account of the various topics has been brought up to date and a new and important chapter on "The Function of Carbohydrates and Glucosides in Plants" has been added. Although other short summaries of our knowledge of the sugars have recently appeared, the monograph under discussion remains much the best and most suggestive account of the subject.

In conclusion, reference may be made to the important question of the

prices of these Monographs on Biochemistry. The present volume, as compared with the first edition, has increased 50 per cent. in size and more than 50 per cent. in price. The effect of such an increase in cost must seriously restrict the circulation of the book and thus defeat one of the main objects of such a series. Moreover, 5s. net appears to be a rather excessive price for a book in which the text extends only to 133 pages, the remainder being bibliography. The reviewer recommends this question to the serious consideration of both editors and publishers.

Complex Ions in Aqueous Solution. By ARTHUR JAQUES, D.Sc., F.I.C. (London, 1914: Longmans, Green & Co. Pp. viii + 151. Price 4s. 6d. net.)

This book aims at giving an account of the subject of complex ions in aqueous solution from the experimental standpoint. The first six chapters contain a discussion of the chief methods used in this field of investigation, and the last four chapters are devoted to examples, including the copper, cobalt, and ammoniacal salt solutions, in which the applications of the various methods are illustrated.

In most respects the author has performed his task well. The book is clearly written, the examples are well chosen, and due attention is paid to matters which require further investigation. The omission of a discussion of theories of valency in a work of this character has much to recommend it, but a fuller discussion of Abegg and Bodländer's views on electroaffinity would have been desirable. The least satisfactory section is Appendix I on the hydrate theory, which affords evidence that the author's knowledge of this subject is inadequate. For example, one and a half pages are devoted to the method tentatively put forward by Philip some years ago of calculating degrees of hydration of solutes from the diminution in the solubility of gases due to the presence of these solutes, although it has been shown by Rothmund,* Müller,† and others that the results obtained by this method are erroneous. The publisher's part of the work is very well done.

The Fixation of Atmospheric Nitrogen. By JOSEPH KNOX, D.Sc. (London, 1914: Gurney & Jackson. Pp. v + 112. Price 2s. net)

This book belongs to the series of monographs edited by Dr. Cumming, of which only two or three have so far appeared. The volumes are well printed, adequately bound, and commendably cheap. The one now under discussion is divided into three sections, dealing respectively with the fixation of atmospheric nitrogen as nitric and nitrous acids, as ammonia and ammonium compounds, and as compounds (such as cyanamides) which readily yield ammonia. The style is clear, and Dr. Knox has succeeded in compressing all the essential facts in comparatively small compass. The book contains a good bibliography and can be heartily recommended.

Intermetallic Compounds. By CECIL H. DESCH, D.Sc., Ph.D. (London, 1914: Longmans, Green & Co. Pp. vi + 113. Price 3s. net.)

Within the last few years a great deal of work has been done on the constitution of alloys, with particular reference to the existence of chemical compounds, and the time had arrived when a brief account of the methods employed and the results obtained in these investigations was very desirable. This need is satisfied in all respects by Dr. Desch's excellent monograph. The description of the methods is clear and concise, and the results obtained up to date are fully described. The chief feature of the book is, however, to be found in the critical discussion of the validity of the results obtained and the

* *Zeitschr. physikal Chem.*, 1909, **69**, 523. † Ibid. 1912, **81**, 483.

indication of possible sources of error, so that the monograph is not merely a compilation of the data to be found in the literature, but forms a valuable and suggestive contribution to a subject of the highest importance. To all who are interested in this branch of chemistry Dr. Desch's monograph can be recommended without reserve.

Telegraphy. By the late Sir W. H. PREECE and Sir J. SIVEWRIGHT. Revised and partly rewritten by W. Llewellyn Preece. (London, 1914: Longmans, Green and Co. Pp. 422, 256 figures. Price 7s. 6d. net.)

There is little doubt that during its very long career Preece and Sivewright's "Telegraphy" has been the most widely read book on the subject in the English tongue, and the new edition of this work now before us upholds in every way the high tradition of its predecessors for general "readability" and lucidity of style.

The book has been enlarged in form and also in subject-matter by the inclusion of chapters on Secondary Batteries and the Baudot System—a welcome addition. A short comparison of various high-speed systems has also been added, while the section on submarine telegraphy has been cut out. In his preface, the Reviser is careful to explain that the work has ceased to be a description of the practice of the British Post Office, as it originally was. This deviation has, indeed, become more and more marked in the last few editions, and in our opinion it is wholly good for this to have occurred. The Post Office practice has, of necessity, become specialized, and it is fortunate that the book has not become a specialist's manual: it has successfully preserved its character as an all-round text-book dealing with the broad fundamental principles of the subject. The Reviser's hope that the book will be of service to those concerned with telegraphy in the Colonies away from home practice will, we think, be amply fulfilled.

The Year Book of Wireless Telegraphy and Telephony for 1914 published by the Marconi Press Agency, Ltd. (Price 2s. 6d.), is a model of its kind. The compilers seem always to have borne in mind that those who consult it may be far from other works of reference, and they have omitted no information that can by any possibility be of use to the wireless engineer or operator. The regulations made by every country in the world are all given.

There is a complete tabulated list of all stations throughout the world with all necessary information as to their working and charges.

A very lucid article by Dr. Fleming on "Waves and Wave Motion" is a model its kind for this class of publication.

Other Technical Articles include: "The Function of the Atmosphere in Transmission," by Dr. Erskine-Murray; "The Measurement of the Strength of Wireless Signals," by Dr. Marchant; "Problems of Wireless Telephony," by C. E. Prince; "The Application of Wireless Telegraphy to Meteorology," by the Superintendent of the Forecast Division of the Meteorological Office; "Wireless Time Signals and Longitudes," by A. B. Hinks, F.R.S. The table of Useful Formula is particularly complete, and includes such diverse formulæ as the "Velocity of Propagation and Wave-length" and the safe h.p. for shafting.

The glossary is well done and there is a dictionary of Technical Terms in five languages. Altogether a well-thought-out book, and one on which its compilers are to be congratulated.

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Transactions

OF

The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. X. MAY, 1915. PARTS 2 AND 3.

THE ANODIC BEHAVIOUR OF ALKALINE BORATE AND PERBORATE SOLUTIONS.

BY WILFRID GUSTAV POLACK.

(*A Paper contributed to the* TRANSACTIONS *of the Faraday Society, September*, 1914.)

Perborates were first prepared in the pure state in 1898 by Melikoff and Pissarjewski,* and by Tanatar.† The one commonly prepared is the sodium salt $NaBO_3 \cdot 4H_2O$, this formula having been established by the above authors and confirmed later by Constam and Bennet,‡ who concluded from conductivity measurements that it is a salt of a monobasic acid, HBO_3. It contains 10·38 per cent. of active oxygen, corresponding with one atom of oxygen in the formula, sodium metaborate being formed by its reduction. It is generally prepared by the action of H_2O_2 or Na_2O_2 on borax solutions, and on account of its oxidizing properties it finds increasing commercial application for bleaching and for laundry work. For such purposes an electrochemical method of preparation would be of value if it could be arranged as a continuous process, after the manner of the hypochlorite electrolysers in use, fresh bleaching solution being drawn off as required and spent liquor returned to the cell, and such an apparatus has been described in a French patent, to which further reference will be made.

On this account an investigation of the electrolytic preparation of perborates appeared to offer an interesting field, especially as the only evidence hitherto available regarding the possibility of preparing perborates electrochemically is of a somewhat unsatisfactory nature.

Tanatar § states that he obtained sodium perborate by electrolysis of a concentrated solution of sodium orthoborate, but gives no details of the process. Later Tanatar ‖ states that perborates are decomposed by the passage of the electric current. Constam and Bennet ¶ describe an experiment in which the anolyte, consisting of 20 grams borax and 4 grams NaOH in 60 c.c. of water, was contained in a Pukall cylinder which dipped into 10 per cent. NaOH as catholyte. They passed 0·5 ampere for 4 hours at a temperature

* *Ber.*, **31**, 678 (1898).
† *Z. Phys. Chem.*, **26**, 132 (1898).
‡ *Z. Anorg. Chem.*, **25**, 265 (1900)
§ Loc. cit.
‖ *Z. Phys. Chem.*, **29**, 162 (1899).
¶ Loc. cit.

of 4° to 6·5° C., but obtained no perborate, or at most a very small quantity (which they called H_2O_2), the oxygen evolved being practically equivalent to the total current. Like Tanatar, they omit all mention of such important factors as electrode material, current density, etc. Bruhat and Dubois * state that sodium perborate can be obtained by electrolysis of a solution of sodium orthoborate, but it is not clear whether they mean to imply that they themselves have prepared it by this method.

The only other evidence is that of a French patent by Pouzenc,† and two articles thereon by Beltzer ‡ in French technical publications. The full details of these were not available when the present work was commenced, but it was known that the apparatus described consists of a vertical electrolyser divided into anode and cathode compartments by a vertical diaphragm, the electrodes being of polished platinum. The electrolyte used for making bleaching solutions is said to contain 24 grams borax + 6 grams NaOH per litre, and is cooled in a reservoir and allowed to flow through the cell, the current density being about 30 to 60 amperes per sq. dm. Later on an opportunity occurred of consulting the original patent and the papers referred to, and they will be discussed in the appropriate place below.

As regards the mechanism whereby sodium perborate might be produced electrolytically, Tanatar suggested oxidation of the borate by H_2O_2 formed at the anode by discharge of OH′ ions thus :—

$$2OH' \longrightarrow H_2O_2 + 2\theta.$$

Riesenfeld and Reinhold,§ however, have shown that even under what they consider the most favourable conditions for this reaction (high alkali concentration, low temperature. and high current density) no H_2O_2 is obtained at the anode from NaOH, and with KOH at 0° C. the concentration only reached 1/1,000 molar after electrolysing for 2 hours with a current density at the anode of 33 amperes per sq. dm. Constam and Bennet make the remarkable statement that, since sodium perborate undoubtedly has the simple formula $NaBO_3$, one would not expect it to be formed electrolytically, because it could not be formed like persulphates or percarbonates by the union of discharging anions. Apparently they were unacquainted with the simple process of anodic oxidation, and there appears to be no good reason why, if sodium perborate can be produced electrolytically, it should not be by simple removal of negative charges, thus :—

Anode—

$$BO_3''' \longrightarrow BO_3' + 2\theta,$$

Cathode—

$$2H_2O \longrightarrow 2OH' + H_2 + 2\oplus\ ;$$

together—

$$BO_3''' + 2H_2O \longrightarrow BO_3' + 2OH' + H_2\ ;$$

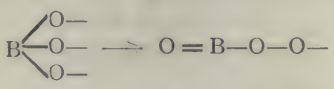
or, writing in the sodium—

$$Na_3BO_3 + 2H_2O \longrightarrow NaBO_3 + 2NaOH + H_2$$

as the total result of the electrochemical process. The removal of negative charges might, of course, take place actually through the intermediate action of an "oxygen-charged" electrode, and not directly, ‖ as shown. Besides

* *Compt. Rend.*, **140**, 506 (1905). † French Patent, No. 411,258 (April, 1910).
‡ *Revue d'Electrochimie*, **5**, 1 (1911) ; *Le Moniteur Scientifique*, 1911, p. 10.
§ *Ber.*, **42**, 2977 (1909).
‖ Cp. Grube on oxidation of ferro- to ferri-cyanides, *Z. f. Elektrochem.*, **18**, 189 (1912).

the loss of negative charges the BO_3''' ion would presumably undergo a structural change thus :—



Perborate ions might also conceivably result from anodic oxidation of various borate ions other than BO_3'''.

Whatever the mechanism, the conditions to be aimed at are those which lead to a high anodic potential, viz., polished platinum anode, at which the overvoltage is known to be higher than at any other, low temperature, and high current density. Low alkali concentration, by diminishing the tendency for discharge of hydroxyl ions, will also favour a high potential. Also, of course, a reasonably high borate concentration is desirable. In practice the simultaneous realisation of these conditions is somewhat difficult.

Detection and Estimation of Perborate.

Sodium perborate in solution can be titrated in presence of H_2SO_4 with permanganate, and behaves like H_2O_2 towards this reagent, two molecules of $KMnO_4$ corresponding to five of $NaBO_3 \cdot 4H_2O$. A sample obtained (as a white powder) from Kahlbaum was found on titration with $KMnO_4$ to contain only about 87 per cent. of $NaBO_3 \cdot 4H_2O$, which, however, on recrystallising, increased to 98 per cent. Numerous titrations with varying quantities of perborate and acid showed the permanganate method to be sufficiently reliable. In a 2 per cent. solution the perborate was found to decompose spontaneously at the rate of about 1 per cent. per hour at ordinary temperature.

Cooling Arrangements.

It is difficult to arrange an apparatus with the anode and cathode as close together as would be desirable, while still separating them by a suitable diaphragm and accommodating the necessary thermometer, etc., and the resistance due to the comparatively low conductivity of the solutions is further increased by the diaphragm and the gas evolution at the electrodes. It was therefore necessary in practically all the experiments, in order to keep the anolyte at the low temperature desired, to use a somewhat elaborate arrangement. A cooling liquid at — 16° C. to — 18° C. was prepared in a large cylindrical metal tank of 24 litres capacity by mixing crushed ice and salt with the necessary amount of water. The metal tank was contained in an outer vessel of earthenware standing on the floor. The liquid was sucked by means of a water-pump through a wire-gauze strainer, and then through the cooling coils in the electrolysis cell into a large glass bottle standing on the bench, with taps so arranged that from an outlet near the foot of the bottle the liquid could, when desired, be run straight back to the tank for further use, without interrupting the flow of cooling liquid through the apparatus.

First Form of Apparatus.

The first cell employed consisted of an outer glass vessel which contained the catholyte, and in this glass vessel stood a porous pot* which contained the anolyte. In order that the gas evolved might be collected, the pot was closed with a rubber stopper fitted with a delivery tube, and fixed through the stopper were also a thermometer, the ends of a glass spiral for cooling the anolyte, an inlet for running in NaOH from a burette, and the anode itself. The last consisted of strips of platinum wire or foil of suitable size to

* The porous pots and tubes used were made thinner and more uniform by grinding them on the lathe with emery.

give the desired current density, and bent outwards so as to lie near the cooling spiral. The cathode consisted of a cylindrical sheet of nickel encircling the pot, leaving only sufficient space between for gas to escape freely. The top of the pot where it projected out of the liquid was waxed to make it airtight.

Composition of the Anolyte.

It appeared desirable in the first instance to try the solution of Pouzenc referred to above, viz., 24 grams borax + 6 grams NaOH per litre. Such a solution, however, was found to have too low a conductivity, the consequent heat evolution being excessive, and solutions were therefore used which contained more NaOH. As pointed out above, however, it is desirable, in order to get a high anodic potential, to keep the alkali concentration as low as possible, but suitable solutions cannot be obtained by merely dissolving larger amounts of borax in water, because 100 grams of water dissolve at 0° C. only 2·83 grams of borax ($Na_2B_4O_7 \cdot 10H_2O$) and at 10° C. 4·65 grams. Potassium borate was found to offer no great advantage in this respect, but by adding KOH a solution could be prepared which contained 27·4 grams K_2O and 50·7 grams B_2O_3 per litre (against 8·8 grams per litre of B_2O_3 in the Pouzenc solution), and such a solution, slightly diluted, was used in one case. Similarly with borax the concentration can be increased by adding NaOH (cp. Constam and Bennet, above). Thus a solution containing 80 grams borax + 20 grams NaOH per litre (29·3 grams per litre of B_2O_3) does not deposit any solid at 0° C., but in the earlier experiments with such solutions less ozone was produced than in other cases, and this was taken as an indication that the anodic potential was lower, and the conditions therefore less favourable, the alkali concentration being apparently too high. Later on it appeared that other factors are probably of greater importance, and that, moreover, the ozone production is a rather uncertain quantity and depends on various things. Of course in one respect an increase in the proportion of alkali might possibly be advantageous by increasing the concentration of BO_3''' ions. Apparently, however, the number of BO_3''' ions present in any alkaline borate solution is very small, the chief ion being probably H_2BO_3'. The composition which would nominally correspond to orthoborate would require, roughly, equal weights of borax and NaOH, but such solutions are very strongly alkaline owing to hydrolysis; in fact, according to Kahlenberg and Schreiner* practically all the excess of NaOH above that corresponding to metaborate is present in the free state, the solution being therefore no richer in BO_3''' ions than a less alkaline one.

The first few experiments showed that it was necessary to add a little NaOH to the anolyte from time to time to compensate for that removed by the electrolysis, otherwise the voltage across the cell rose rapidly. In some cases it was even necessary to add a little at the commencement in order to reduce the high resistance and consequent great heat evolution.

Experiments with First Form of Cell.

Some experiments with the first form of cell are briefly summarised in Table A. The first two columns give the composition of the anolyte in grams per litre of borax and caustic soda. The symbols used are as follows throughout the paper :—

T = Temperature of the anolyte.
C = Current through cell (in amperes).
D_A = Current density at anode in amperes per sq. dm.
V = Voltage across cell.

* *Z. Phys. Chem.*, **20**, 547 (1896).

TABLE A.

	Borax.	NaOH.	T.	C.	D_A.	V.	Time
1	29 gm.	18 gm.	4° to 5° C.	4·0	22	8·8 to 10·4	45 min.
2	24 „	17 „	−2° C.	4·0	73	10·4	35 min.
3	80 „	20 „	0° to −1° C.	3·3	60	11·2 to 8·0	2 hr.
4	80 „	20 „	−1° to −2° C.	3·5	106	11·6 to 9·6	1 hr.

The catholyte in each case was 4 per cent. NaOH. These and other similar experiments (in one case using potassium borate) gave negative results. The rate of evolution of oxygen was measured occasionally during each experiment and always corresponded as closely as could be ascertained to the total current. After each experiment the anolyte was tested with

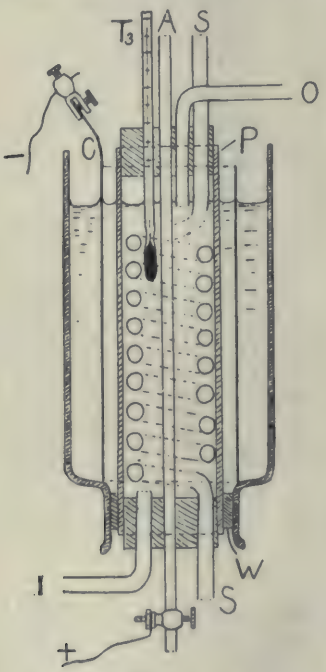


FIG. 1.

$KMnO_4$. In no case was there any oxidising action except in No. 3, when 10 c.c. of anolyte decolourised one single drop of N/4 $KMnO_4$.

The only hope of obtaining more favourable conditions appeared to lie in the employment of a cooled anode. Although the bulk of the liquid in some of the above experiments was at a temperature in the neighbourhood of zero, the portions surrounding the anode might be at a considerably higher temperature owing to the high anodic current density, and it seemed that by using a cooled anode this condition might be more or less reversed, the liquid in contact with the anode being kept at a sufficiently low temperature, while the bulk of the electrolyte need only be kept at a moderately low temperature. Thus Prausnitz * was able to obtain very satisfactory yields of

* *Z. f. Elektrochem.*, **19**, 676 (1913).

hypochlorite by employing a cooled anode, even when at the same time the bulk of the liquid was actually warmed to reduce the potential drop. Moldenhauer,* who gives a theory of heat evolution at the electrode surface, obtained improved yields in various electrolyses. Cooled anodes have also been used in the preparation of persulphuric acid from sulphuric acid for the manufacture of hydrogen peroxide.

The anode used in the apparatus to be described consisted of a platinum tube† 20 cm. long, 3 mm. external diameter and 0·17 mm. in thickness, the area of the portion actually immersed in the electrolyte being approximately 8 sq. cm.

Cooled Anode Apparatus.

The electrolysis cell is shown in Fig. 1 in section. P is a porous tube of 3 × 12 cm., held in place by the rubber washer W. S is the cooling spiral,

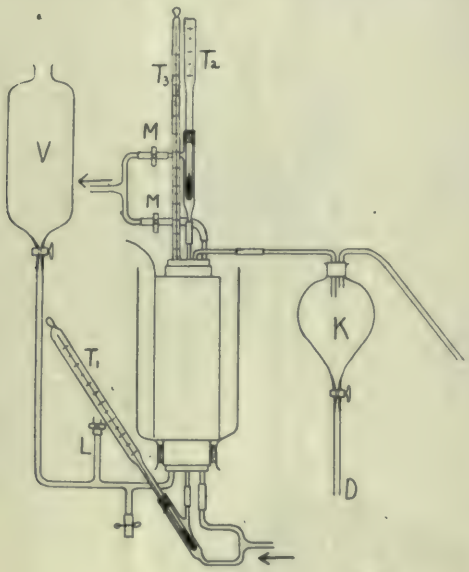


FIG. 2.

A the anode, T_3 a thermometer, and C the cathode, a cylindrical sheet of nickel as before. The outer glass vessel served to contain the catholyte. The anolyte flowed in at I and gas and liquid came out at O.

The general arrangement of the apparatus is shown in Fig. 2. The vessel V contained the anolyte (generally about 100 to 125 c.c.), the tap regulating its flow to the anode compartment. Gas and liquid collected in K, the former passing on through the delivery tube, while the latter could be drawn off at D and returned to V, a continuous circulation of the anolyte being maintained. A burette containing NaOH was connected at L, a few c.c. being run in as required. The cooling liquid, which entered at the foot

* *Z. f. Electrochem.*, **11**, 307 (1905).

† An attempt was made to use an anode of platinised brass tube. The platinising was carried out with the citrate solution of Langbein (*vide* Schlötter's *Galvanostegie*, p. 187), the tube being rotated in the liquid. It was found possible by this means to obtain an excellent platinum surface, which could be well polished and was highly resistant mechanically; but unfortunately when used as anode in alkaline solution at high current density it rapidly disintegrated, cupric hydroxide being ultimately found in the liquid.

as shown by the arrows, was divided between the anode and the glass spiral, the proportion being regulated by the screw clips M.

No electrical leakage took place through the salt solution flowing through the anode; in some cases two ammeters were connected in the circuit, one on each side of the cell, and these agreed perfectly.

The thermometers T_1 and T_2 give the temperature of the liquid entering and leaving the anode.* The mean of these is the nearest indication that can be obtained of the actual temperature of the anode and is given as T_A below.

T is the temperature of the anolyte, as given by thermometer T_3. The other letters below have the same significance as before. The catholyte was 4 per cent. NaOH in each case. The composition of the anolyte is stated at the commencement in each case.

Experiments with Cooled Anode Apparatus.

1. *80 grams borax + 20 grams NaOH per litre.*—

$C = 4{\cdot}8$. $D_A = 60$. $V = 18$ to 20.
$T_A = -11°$ C. to $-7°$. $T = 4°$ to $6°$ (finally $15°$).
Time, 1½ hr.

Ozone production very slight.

2. *38 grams borax + 40 grams H_3BO_3 per litre.*†—

$C = 4{\cdot}8$. $D_A = 60$. $V = 25$.
$T_A = -10{\cdot}5°$ to $-5°$. $T = 13°$ to $20°$.
Time, 1½ hr.

Evolved oxygen smelt very strongly of ozone. This anolyte contained more B_2O_3 than No. 1 (37 grams per litre against 29·3), but was much less alkaline; at the commencement it was almost neutral, but was kept faintly alkaline throughout. Although such a solution contains complex anions, it would presumably be capable of furnishing some BO_3''' or other ion necessary for perborate formation.

3. *28 grams borax + 5 grams NaOH per litre.*—

$C = 2{\cdot}4$. $D_A = 30$. $V = 18$ to 15.
$T_A = -13°$ to $-10°$. $T = 4°$ to $0°$.
Time, 1½ hr.

Ozone production slight.

Attempts were also made to employ much higher current densities, but as the current through the cell could not be increased without undue rise of temperature, it was necessary to cover up portions of the anode by means of closely fitting glass tubing, and the uneven current distribution and cooling gave rise to difficulties. In one case, however, it was found possible to carry on the electrolysis for 1 hour at a current density of 200, T_A being $-7{\cdot}5°$ and T about 20°.

The above and all similar experiments also gave negative results, except that in No. 3 the resulting anolyte showed faint oxidizing action, 50 c.c. decolourising 1 drop of N/4 $KMnO_4$.

It appeared therefore desirable to ascertain whether, if sodium perborate were present in the anolyte at the commencement of such an experiment, its concentration would actually diminish.

* The difference between these varied with the rate of flow, but never exceeded $5{\cdot}5°$ C.

† McLaughlan, *Z. Anorg. Chem.*, **37** (1903), 371.

The following experiment was therefore carried out.

4. *28 grams borax + 5 grams NaOH per litre + some perborate.*—

$C = 4{\cdot}8$. $D_A = 60$. $V = 30$.
$T_A = -11{\cdot}5°$ to $-4{\cdot}5°$. $T = 15°$ to $11°$.
Time, 1 hr.

Samples of the anolyte were titrated with $KMnO_4$ solution before and after the electrolysis.

10 c.c. of anolyte required :—

Before, 2·7 c.c. of N/4 $KMnO_4$.
After, only 2 drops of N/4 $KMnO_4$.

Throughout the experiment no ozone could be detected, except a faint trace at the very end.

This experiment was repeated in another form, the perborate being added during the electrolysis instead of before the commencement.

5. *35 grams borax + 5 grams NaOH per litre.*—

$C = 4{\cdot}8$. $D_A = 60$. $V = 35$ to 40.

At commencement—

$T_A = -6°$. $T = 25°$.

After current had been passing for 10 minutes the perborate (0·5 gram dissolved in 35 c.c. of water) was added, T_A being $-6{\cdot}5°$, $T = 16°$. The evolved oxygen smelt strongly of ozone when the perborate was added, but this gradually disappeared, and 10 minutes later no ozone could be detected, although there was no appreciable change in the temperatures, T_A being $-7{\cdot}5°$, $T = 16°$. Samples of the anolyte were titrated from time to time with $KMnO_4$.

Time. (From addition of perborate.)	Titre (10 c.c.). (In c.c. of N/4 $KMnO_4$.)
0 minutes	2·0 (calculated)
25 ,,	1·4
45 ,,	0·7

These experiments suggested that the perborate acts in some way as a depolariser, lowering the anodic potential (which would account for the effect on ozone production) and being itself decomposed. It appeared, however, that probably this is due not to the perborate itself, but to H_2O_2 formed by its hydrolysis. Pissarjewski,* from extraction experiments with ether, concluded that in aqueous solution at 25° C. sodium perborate is almost completely hydrolysed, and he supposes the hydrolysis to take place thus :—

$$NaO_2BO + H_2O \longrightarrow NaO_2H + HBO_2,$$

the sodium hydroperoxide thus formed being further hydrolysed to NaOH and H_2O_2. The hydrolysis might take place in various ways, depending on the conditions, and on what borate ions were produced. Thus in alkaline solution, if BO_3''' were formed, the reaction could be simply represented thus,† omitting the sodium—

$$BO_3' + 2OH' \rightleftarrows BO_3''' + H_2O_2,$$

and apparently the hydrolysis would be less the lower the alkali concentration, *e.g.*, in acid solution (although the perboric acid might then decompose otherwise). Whatever may be the exact mechanism, it is certain that perborates in solution are very largely hydrolysed to H_2O_2. The reaction with

* *Z. Phys. Chem.*, **43** (1903), 170.

† This equation is purely formal, and is not intended to imply any particular "mechanism" of H_2O_2 formation.

permanganate shows this, and a dilute solution of sodium perborate has the characteristic taste of H_2O_2.

If, therefore, in an experiment such as No. 5 above, H_2O_2 be added instead of perborate, one would expect the result to be similar, and this was found to be the case, the ozone production ceasing and the permanganate titre diminishing rapidly. One experiment was continued till the H_2O_2 concentration was vanishingly small, when ozone commenced to be produced again, increasing gradually in strength.

It might be argued that the disappearance of H_2O_2, and therefore of perborate, is due to chemical decomposition, and not to an electrochemical effect as suggested above; but experiment showed that the rate of decomposition of H_2O_2 in a 1 per cent. solution of NaOH is comparatively small at ordinary temperatures, although above 40° C. it increases rapidly. Moreover, an electrolysis experiment with acid (phosphoric) anolyte, which will be described below, gave precisely similar results, and under these conditions the chemical decomposition would be very much slower than in alkaline

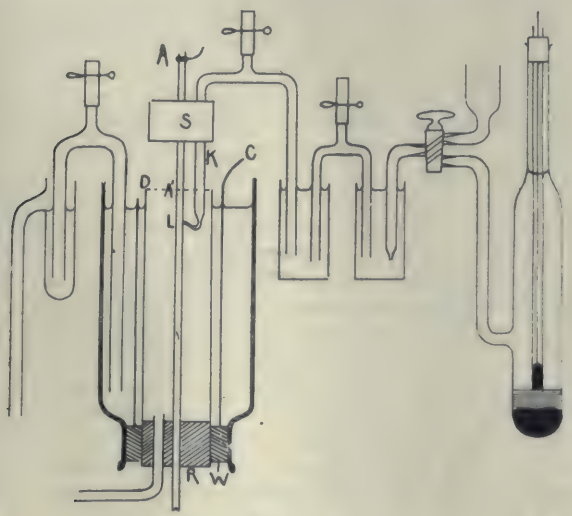


FIG. 3.

solution. The non-production of ozone might also be due to chemical interaction with the H_2O_2,* but it appeared probable that it was chiefly due to lowering of the anode potential. In any case it was thought that actual measurements of the anodic potentials in a few cases would be of interest, especially as no such measurements in alkaline solutions appear to have been carried out hitherto.

Anode Potential Measurements.

The method adopted was to measure a combination of the type

$$\text{Pt anode} \left| \begin{matrix} \text{NaOH} \\ \text{Borax} \end{matrix} \right| \text{NaOH} \left| \text{N/10 NaOH} \right| \begin{matrix} \text{N/10 NaOH} \\ \text{HgO} \end{matrix} \left| \text{Hg} \right.$$

the standard electrode employed being the $\text{Hg} \left| \begin{matrix} \text{HgO} \\ \text{N 10 NaOH} \end{matrix} \right.$ electrode devised by Donnan and Allmand.† The one actually used was made up

* Schöne, *Liebigs Annalen*, **196** (1879), 239.
† *Trans. Chem. Soc.*, **99**, 845 (1911).

precisely according to the directions given by these authors, and was checked by comparison against a similar electrode, its e.m.f. being taken as $E_h = +0{\cdot}168$ volts at the temperature of the laboratory. The e.m.f. of the combination was measured by the potentiometer method, using a standard cadmium cell, an accurate platinum-iridium bridge wire, and a sensitive galvanometer.

The apparatus is shown diagrammatically in Fig. 3, the cell being shown in section. As the chief thing is to maintain a solution of constant composition round the anode, a large volume of electrolyte was contained in a reservoir (not shown in the diagram) of 800 c.c. capacity, and was allowed to flow fairly rapidly into the anode compartment. The anode was the platinum tube used in the previous experiments. The diaphragm D consisted of a sheet of asbestos paper* wrapped round the close spiral used for cooling the anolyte, and fixed at the foot between the rubber stopper R and the rubber washer W. The liquid entered the anode compartment at the foot and flowed partly through and partly over the asbestos (the anode compartment being open at the top) into the cathode compartment, from which it overflowed by means of the syphon, the side tube being introduced to keep the level constant. The cathode C consisted, as before, of a cylindrical nickel sheet encircling the anode compartment. The advantage of allowing the electrolyte to flow through both anode and cathode compartments is that its composition (as regards borate and alkali) remains unaltered, and it can be returned again to the reservoir. The standard electrode was connected in the usual way through the various intermediate solutions to the glass tube K, which terminated in a small capillary. This tube was held in place by the rubber stopper S, the end of the capillary being pressed firmly against a small flattened portion of the anode. The cooling spiral and the thermometers are omitted from the diagram for convenience.

The potential actually measured is that between the liquid in contact with the anode at L and the top of the anode A. The latter is practically the same as the potential of the anode at L, because no current flows through the portion AA′ (the current entering the foot of the anode) and very little through the portion A′L. The capillary was placed fairly near the surface to minimise the potential drop† between A′ and L.

The first attempts to measure the potential with dilute alkaline borate solutions (such as Pouzenc's) were not successful. The high resistance made the readings difficult, and violent fluctuations occurred. If the specific conductivity of the solution be taken as 0·02 (that of N/10 NaOH) the potential gradient round the anode with $D_A = 38$ would be $0{\cdot}38/0{\cdot}02 = 19$ volts per cm. It is therefore evident that a very minute movement of the capillary might greatly affect the readings.

* This had to be renewed from time to time, as it becomes weakened by the action of the alkaline liquid.

† This can be calculated thus: Assuming the current density to be uniform, the current flowing in the anode at a point x cm. below the surface will be $\frac{x}{l} \cdot C$, C being the total current, and l the length of the anode immersed in the liquid. The potential difference between this point and the surface will therefore be $\int_l^x C \cdot R \cdot dx$ (where R is the resistance of unit length of the anode), which becomes $\frac{C R}{2 l} \cdot x$.

With the capillary 15 mm. below the surface, and C = 5 amperes, this becomes 0·5 millivolts, which is negligible. If, however, the capillary were half-way down, the value would be 3·5 millivolts.

Later on it was found possible, by fixing the capillary more rigidly, and shaping it in such a manner as to prevent gas bubbles collecting in it, and by using a more sensitive galvanometer, to obtain satisfactory measurements with such a solution. In the first instance, however, more alkaline solutions were used, and the readings with these were very satisfactory, the relative error of any one measurement being not more than a few millivolts.

The exact values, however, in a given case are not reproducible, as they depend on the precise condition of the anode surface at the given moment.

The method adopted to find the effect on the potential of adding H_2O_2 to the electrolyte was to wait until the potential was constant, or at least not rising rapidly, then to add the requisite number of c.c. of concentrated H_2O_2* to the liquid in the reservoir. When it was desired to continue the measurements for a considerable time, the solution issuing from the cell was rapidly titrated, H_2O_2 added to restore the original concentration, and the liquid poured back into the reservoir.

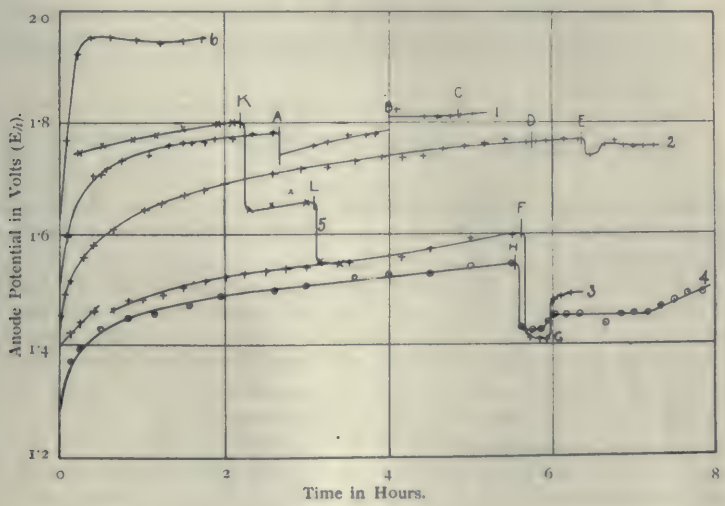


FIG. 4.

The chief measurements carried out are shown graphically in Fig. 4, the numbers on the curves corresponding with the numbers below.

The liquid potentials—

$$\text{NaOH conc. } C_1 \mid \text{NaOH conc. } C_2$$

were calculated from the formula

$$e = (2v - 1)\ 0{\cdot}058 \log C_1/C_2,$$

neglecting the difference in ionisation at the two concentrations.

The liquid potential in such cases as—

$$\begin{matrix}\text{NaOH conc. } C_1 \\ \text{Borax}\end{matrix} \Big| \ \text{NaOH conc. } C_1$$

was neglected. For the present purpose the absolute values within 10 or 20

* Merck's *Perhydrol* (diluted).

millivolts are of no importance. Slight fluctuations of the potential are probably largely due to variations in the rate of flow of the electrolyte, which may cause variations in the local concentration round the anode.

In Nos. 1 to 4 the anode was not cooled, the anolyte being cooled by means of iced water. In Nos. 5 and 6, both anode and anolyte were cooled with freezing mixture, as in the former experiments.

1. *N. NaOH + 35 grams borax per litre.*—

Temp. 10°C. $D_A = 38$.

Anode | N. NaOH, Borax | N. NaOH | N/10 NaOH | N/10 NaOH, HgO | Hg.

This curve shows the rapid rise at the commencement, and the effect of altering D_A.

At—

A (2 hr. 40 min.) D_A was reduced to 19.

B (4 hr. 0 min.) D_A was raised again to 38.

C (4 hr. 50 min.) H_2O_2 was added to the electrolyte to make 0·01 Molar (·34 gram per litre), but there was no effect on the potential.

2. *N. NaOH.*—

$T = 10°$. $D_A = 38$.

Anode | N. NaOH | N. NaOH | N/10 NaOH | N/10 NaOH, HgO | Hg.

Omission of the borax would presumably have no great effect on the potential and would simplify the conditions, as there will only be H_2O_2 and no perborate present.

At D (5 hr. 45 min.), H_2O_2 added to make 0·01 M., but there was no effect on the potential. At E (6 hr. 22 min.), H_2O_2 made 0·10 M. Potential fell slightly, viz. from 1·770 to 1·740, then rose again to 1·766, although the concentration was maintained. After this experiment, the anode, which was used without cleaning or polishing in any way after No. 1 (i.e. some 12 hours at 38 amperes per sq. dm.) had acquired a brownish colour. This appearance had been noticed before, but never to the same extent. It was carefully rinsed with water (to remove all H_2O_2) and gently rubbed on a piece of filter paper, moistened with KI and starch, a deep blue stain being produced. This indicated the presence on the anode surface of one of the higher oxides of platinum.

The next experiment was carried out at a much lower current density, as it appeared probable that under these conditions the effect of H_2O_2 on the potential might be more marked.

3. *N. NaOH.*—

$T = 10°$. $D_A = 3·8$.

Freshly polished anode.

Anode | N. NaOH | N. NaOH | N/10 NaOH | N/10 NaOH, HgO | Hg.

The irregularities at the commencement were caused by a defective connection, with consequent fluctuations and momentary stoppage of the current. At F (5 hr. 37 min.), H_2O_2 added to make 0·077 M. Potential fell from 1·595 to 1·407, then remained steady till the reservoir was refilled (no further H_2O_2 being added, its concentration being now 0·059 M. The potential then rose (G 6 hr. 0 min.) to a higher value.

4. Same as No. 3, only adding sodium perborate instead of H_2O_2. The method adopted was to select a moment when the reservoir was just becoming empty, and fill it up with a solution of the same composition, but containing in addition the necessary quantity of perborate, the concentration of the latter being such that if completely hydrolysed it would give approximately the same H_2O_2 concentration as in No. 3; i.e. the $KMnO_4$ titre was approximately the same.

At H (5 hr. 32 min.) the perborate was added (to make 0·070 M.).

The potential fell from 1·544 to 1·432. After 6 hr. 10 min. the titre was maintained constant by adding H_2O_2, but the readings fluctuated somewhat.

5. *8 grams NaOH + 35 grams borax per litre.*—
Cooled anode.

$$D_A = 50$$

i.e. a solution similar to those used in the electrolysis experiments and under similar conditions.

$$\text{Anode} \left| \begin{matrix} \text{N/5 NaOH} \\ \text{Borax} \end{matrix} \right| \text{N/5 NaOH} \left| \text{N/10 NaOH} \right| \begin{matrix} \text{N/10 NaOH} \\ \text{HgO} \end{matrix} \left| \text{Hg.} \right.$$

Temperature of anolyte varied between 13·5° and 17°.
Temperature of anode varied between −4° and −6°.

No readings were obtained at the commencement.

At K (2 hr. 12 min.), H_2O_2 added to make 0·095 M. Potential fell from 1·797 to 1·644, then rose slowly until at L (3 hr. 5 min.) the H_2O_2 concentration was doubled (0·19 M.). Potential then fell from 1·655 to 1·550, the drop being nearly the same as at K.

6. *4 grams NaOH + 35 grams borax per litre.*—
Cooled anode (freshly polished).

$$D_A = 50.$$

$$\text{Anode} \left| \begin{matrix} \text{N/10 NaOH} \\ \text{Borax} \end{matrix} \right| \text{N/10 NaOH} \left| \begin{matrix} \text{N/10 NaOH} \\ \text{HgO} \end{matrix} \right| \text{Hg.}$$

Temperature of anolyte, 15° to 19°.
Temperature of anode, −4° to −8°.

The potential rose very rapidly at first, owing presumably to the high current density and freshly polished anode. The high value reached ($E_A = 1·953$) is probably also due to the low alkali concentration. The subsequent slight fall may be due to temperature variation.

No H_2O_2 or perborate was added.

No conclusions were drawn from these experiments as regards ozone evolution. The form of the apparatus made it more difficult than in the case of the electrolysis experiments to determine whether ozone were present or not, and it was detected with certainty only in the case of No. 1, and in this case it vanished on the addition of H_2O_2, although the potential remained the same.

The above measurements, together with the previous experiments on the diminution of the H_2O_2 concentration, show that H_2O_2 placed round a polished platinum anode which is strongly polarised tends to lower the potential, the actual drop depending on the various conditions, while the H_2O_2 itself is destroyed.

These facts are in accordance with the theory, which is now generally accepted, that the overvoltage at such a platinum anode is essentially determined by the platinum oxides* contained in the surface layers.

This theory is chiefly due to Grube,† who from measurements of the potentials in H_2SO_4 of electrodes made of various oxides of platinum, concluded that when a platinum electrode is anodically polarised the surface layers contain varying amounts of PtO, PtO_2, and PtO_3 in solid solution. The PtO_3 has a much higher potential than the other two, and the greater its concentration, the higher will be the potential of the electrode.‡ It is formed by oxidation of the PtO_2 by the anodically produced oxygen, but is unstable, and breaks up again into oxygen and a lower, more stable oxide, its final concentration therefore depending on a balance between its rate of production from PtO_2 and its rate of spontaneous decomposition; the greater the former, the higher will be the final PtO_3 concentration, and the greater the anodic potential. The actually observed formation of one of these higher oxides, referred to above under Experiment 2, is of interest in this connection.

Hydrogen peroxide can act electrochemically in two ways, corresponding to its chemical action as an oxidising and a reducing agent respectively.

$$1.\ H_2O_2 \rightleftarrows 2OH' + 2\oplus.$$
$$2.\ H_2O_2 \rightleftarrows O_2 + 2H^{\cdot} + 2\ominus.$$

This was first clearly shown by Haber,§ and was applied by Foerster ‖ to the action of H_2O_2 on a platinum anode, on the theory that an oxide PtO_x was formed, which in the light of the subsequent work by Grube we may call PtO_3.

Foerster's equations then become

$$(a)\ Pt + 3H_2O_2 \longrightarrow PtO_3 + 3H_2O,$$
$$(b)\ PtO_3 + H_2O_2 \longrightarrow PtO_2 + O_2 + H_2O,$$

corresponding to 1 and 2 above.

Most of the experiments which have been carried out by other workers on H_2O_2 potentials are concerned with equilibrium conditions. In the present case, however, H_2O_2 was placed round an anode which was strongly polarised, and in which the PtO_3 content was therefore very high. We should therefore expect action (*b*) to take place, resulting in a lowering of the potential and disappearance of the H_2O_2. Grube found that the rate of self-discharge of his PtO_3 electrodes was greatly accelerated by addition of H_2O_2, the potential falling rapidly; in the present case, however, fresh PtO_3 is continuously being produced, and the actual fall of potential may be comparatively small, as the experiments showed. The final value reached, if the H_2O_2 concentration be maintained, will again represent a state of balance between formation and decomposition of PtO_3 and will depend on the H_2O_2 concentration, the current density, the temperature, etc.

Applying these considerations to the electrolytic preparation of perborates, it appears that, supposing that perborate ions can actually be formed at potentials attainable in practice, the H_2O_2 produced by hydrolysis will have a

* At very low current densities capillary phenomena also play a part.

† *Z. f. Elektrochem.*, **16**, 621 (1910).

‡ When the anodic polarisation is very high, Grube considers that a still higher oxide, probably PtO_4, is also present.

§ *Z. f. Elektrochem.*, **7**, 441 (1901).

‖ *Z. Phys. Chem.*, **69**, 254 (1909).

twofold action. Firstly, it may affect the further formation of perborate by lowering the potential. Secondly, it will be itself destroyed, causing further decomposition of the perborate already formed. As both these effects will increase with increase of the H_2O_2 concentration, an equilibrium concentration of perborate will finally be obtained.

It is probable that the same effect plays a part in the electrolytic preparation of persulphates and percarbonates. Persulphates, however, are only very slightly hydrolysed at ordinary temperatures; percarbonates are certainly considerably hydrolysed, but the conditions under which they are produced (generally from a very concentrated solution of K_2CO_3) are more favourable than in the case of perborates. In the case of persulphuric acid, it is known that the mono-persulphuric acid formed by hydrolysis acts as a depolariser and affects the yield. It is also possible, of course, that persulphates and percarbonates can be produced at lower potentials than perborates.

It was suggested above that the hydrolysis might be less in acid solution. It also seemed probable that higher potentials would be reached in acid solution. An experiment was therefore carried out (No. 1 below) using the cooled anode apparatus, with an anolyte consisting of boric acid in presence of phosphoric acid. Of course it was not expected that free perboric acid would be formed in quantity, but it appeared that the solution might show some oxidising properties.

Further Experiments with Cooled Anode.

1. *N.* H_3PO_4 *(33 grams/litre) + 20 grams* H_3BO_3 *per litre.*—

$C = 2{\cdot}4$. $D_A = 30$. $V = 21$ to 22.

Time, 70 min.

$T = 3°$ to $4°$. $T_A = -9°$.

Samples of the anolyte were tested with $KMnO_4$ 55 and 70 min. from the commencement, but there was no trace of decolourisation.

Hydrogen peroxide was then added to the anolyte to make 0·1 N, (1·7 grams per l.), the temperatures being maintained about $T = 2°$ $T_A = -5°$. In 50 minutes the $KMnO_4$ titre fell from 3·8 to 2·0. This is of interest because in presence of phosphoric acid the chemical decomposition of H_2O_2 is very slight. In this experiment ozone continued to be produced even in presence of the H_2O_2.

It was pointed out above that in the earlier experiments in which the anolyte consisted of excess of borax dissolved in NaOH, the ozone production was very slight. In the light of the information subsequently gained, however, even if the potential in such cases is lower, other advantages might possibly outweigh this. In the first place it appeared that probably the temperature of the anolyte could be kept lower, which would probably tend to diminish the hydrolysis.* The increase in the total borate concentration would also be an advantage. An experiment was therefore carried out (with cooled anode) using the solution of Constam and Bennet (see above) containing 282 grams borax + 56 grams NaOH per litre. Such a solution deposited solid only slowly at 0°C.

As this was the only experiment in which perborate was produced in appreciable, although still very small quantity, it will be given somewhat more fully.

* Pissarjewski, loc. cit.

2. *282 grams borax + 56 grams NaOH per litre.*—
Freshly polished anode.
Catholyte — 8 per cent. NaOH. Vol. of anolyte — 142 c.c.

$C = 4{\cdot}8$, $D_A = 60$ during first 20 min.
$C = 2{\cdot}4$, $D_A = 30$ thereafter, to enable anolyte to be kept at low temperature.

The course of the experiment is shown in tabular form below.

A few c.c. of 16 per cent. NaOH had to be added soon after the commencement to prevent deposition of solid. The titre given is of 10 c.c. of anolyte against N/4 $KMnO_4$. V was 20 to 23 at first. At the lower current density V was 13 to 16.

Time.		Temperatures.		Titre.	Remarks.
Hr.	Min.	T	T_A		
0	0	7° C.	— 14°	0	
0	10	4°	— 12·5°	—	NaOH added. Ozone distinct
0	20	—	—	1 drop	C reduced to 2·4
0	40	2·5°	— 9·5°	2 drops	Still ozone
1	0	0°	— 9·0°	2 drops	Ozone less strong
1	45	—1°	— 7·5°	0·26 c.c.	No ozone
2	20	0°	— 9·5°	0·30 c.c.	,,
2	40	0°	— 8·5°	0·35 c.c.	,,
3	0	0°	— 5·0°	0·38 c.c.	,,

The final concentration of perborate represents a chemical yield of about 0·15 per cent. and a current efficiency of about 0·48 per cent. It must be remembered, however, that only about one-third of the anolyte is actually in the cell at a given moment, the whole being kept in constant circulation through the cell. The exact significance of these figures is therefore doubtful.

Constam and Bennet, as stated above, also obtained some decolourising effect on $KMnO_4$ as the result of their experiment, but said that it was due to production of H_2O_2. As there will presumably be an equilibrium between H_2O_2 and perborate, their reason for making this statement is not clear.

One further experiment was performed with the cooled anode apparatus to determine whether under the conditions of the above experiment, if the perborate concentration in the anolyte were comparatively high, it would tend to diminish.

3. At the commencement the anolyte was identical with that in the last experiment, but only half the quantity was placed in the reservoir, the remaining half, containing perborate, being added only after some perborate had been formed in the cell. By this method it was ensured that the conditions were as favourable for perborate formation as in the previous case. The temperatures, etc., were as nearly as possible the same as in No. 2 ; D_A was 30 from the commencement, the anode being again freshly polished. As before, a little NaOH had to be added to prevent crystallization, but the amount added after the addition of perborate, to compensate for that removed by electrolysis, did not exceed 5 c.c., so no appreciable error is caused in the titrations on this

account. Time was allowed for the perborate to become uniformly distributed throughout the anolyte before any titrations were made.

Time.		Temperatures.		Titre.	Remarks.
Hr.	Min.	T	T_A		
0	0	7° C.	— 13·5°	0	—
0	15	—	—	0·13 c.c.	Ozone distinct. NaOH added.
0	20	3°	— 11°	—	Ozone strong.
0	20	—	—	—	Remainder of anolyte + perborate added.
0	30	4°	— 10°	—	Ozone very faint.
0	40	—	—	4·20 c.c.	—
1	0	3°	— 9·5°	3·64 c.c.	No ozone.
1	15	0°	— 8°	3·18 c.c.	,,
1	25	0°	— 7·5°	2·89 c.c.	,,
1	43	1°	— 8°	2·52 c.c.	,,

The titre given in this case is of 2 c.c. against N/10 $KMnO_4$.

From these figures, and those in the previous experiment, it appears that the equilibrium concentration which would finally be obtained would be very low, probably not very much greater than that actually reached in No. 2 (after electrolysing for nearly 3 hours) which represents a very small yield indeed.

It is possible that better results might be obtained by the use of still more concentrated solutions (if such can be obtained) and still lower temperatures; or by the use of solutions containing a larger proportion of alkali, which may possibly contain more BO_3''' ions, but the experiments have not so far been extended in these directions, nor does it seem probable that satisfactory yields would be obtained under any conditions.

The Pouzenc Patent.

Under these circumstances it is difficult to account for the existence of the French patent by Pouzenc referred to above. Reference to the patent specification revealed the fact that it contains only a brief description of the apparatus, consisting of the vertical electrolyser referred to above. The two papers by Beltzer, however, were found to contain various details, some of which have already been given. According to these, solid perborate* can be obtained by filtering the liquid flowing out of the anode compartment of the Pouzenc cell, the filtrate being mixed with the catholyte and used again. Beltzer says that for preparation of solid perborate it is best to use a "concentrated solution of sodium orthoborate," while for making bleaching solutions he recommends the solution containing 24 grams borax + 6 grams NaOH per litre, which he ascribes to Pouzenc. He also states that the electrolyte must flow rapidly through the cell, and that the solid perborate must be removed immediately from the action of the current and the alkaline liquid, otherwise it "redissolves in the liquid and decomposes."

As a matter of fact, from the diagrams of the apparatus it seems that the

* According to Melikoff and Pissarjewski 100 grams H_2O dissolve 2·55 grams $NaBO_3 \cdot 4H_2O$ at 15° C., so if good yields were obtained solid would separate.

amount of liquid actually in the cell at a given moment is comparatively small; in other words the "current-concentration" is high. Such a condition is necessary in cases where the product is chemically unstable, e.g. in the case of hyposulphites; but it has been shown that the important factor in the case of perborates is the electrochemical decomposition.

As regards temperature, $-5°$ C. is mentioned by Beltzer, but it is not clear whether this is meant to refer to the electrolyte itself, or the brine used to cool it.

In one of the papers a commercial form of the apparatus is described, but it is clearly stated at the commencement that the electrochemical method was not so far (1911) used for the manufacture of perborates, and a careful study of the papers gives the impression that the author has not actually carried out any experiments on the subject.

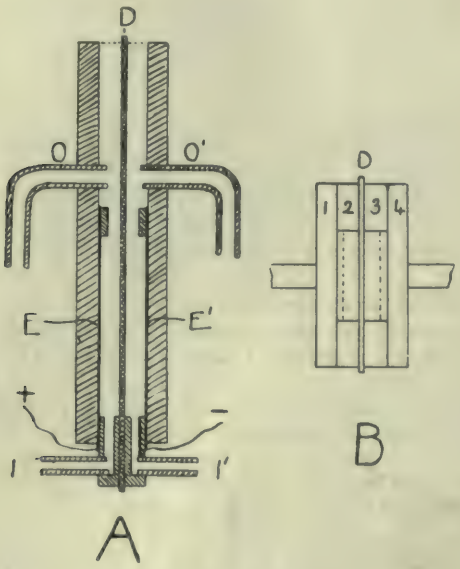


FIG 5.

Experiments with the Pouzenc Apparatus.

A small cell constructed to imitate as nearly as possible the Pouzenc electrolyser on a small scale is shown in Fig. 5.

A is a vertical section through the middle of the cell. B is a plan of the top of the cell. It was constructed of four portions of ebonite sheet (numbered in the diagram) which were clamped together by large clamping screws (not shown in the diagram), thin rubber washers being interposed to make the cell watertight. The electrodes of fairly stout and well-polished platinum foil, shown in the diagram by the dark lines E and E', were fixed between 1 and 2 and 3 and 4, the diaphragm D of asbestos paper being between 2 and 3. The electrolyte entered the anode and cathode compartments, which were identical, at I and I', and overflowed a little above the tops of the electrodes at O and O', the part of the cell above that serving as a settling chamber for

spray. The inlet and outlet tubes were of glass, fixed in by a suitable cement.

The dimensions of the cell were as follows :—

Area of electrodes	8 sq. cm. each.
Distance apart	12 mm.
Volume of anolyte	5 c.c.
„ catholyte	„

The electrolyte was contained in a glass reservoir in which it was cooled by glass spirals through which flowed the usual cooling liquid. Separate glass tubes conveyed it to the anode and cathode chambers, the rate of flow through each being separately regulated by screw clips. The glass tubes were as short as possible, and well lagged, to prevent access of heat.

Experiments were first carried out with the Pouzenc solution, containing 24 grams borax + 6 grams NaOH per litre. With 2 amperes passing through the cell ($D_A = 25$) the voltage across the cell was 25, and although the solution was cooled almost to its freezing-point (— 0·89° C.) the anolyte leaving the cell had a temperature of 17° C. It was tested with $KMnO_4$, but showed no trace of oxidising action. It is difficult to imagine that such a solution could be used commercially, as the heat produced in the cell, and the power absorbed, would be excessive. Determination of its conductivity showed the latter to be, at—

$$0° \text{ C. } k = 9{\cdot}02 \times 10^{-3},$$
$$18° \text{ C. } k = 14{\cdot}87 \times 10^{-3}.$$

This is less than the conductivity of an N/10 solution of NaOH, which has a conductivity of about 20×10^{-3} at 18°.

Experiments were then carried out with a solution whose composition corresponded to sodium orthoborate. The electrolyte consisted of a large volume (1 litre) of a solution containing *95·5 grams borax + 100 grams NaOH per litre*,* cooled to about — 5° C. It was very strongly alkaline. Experiments were carried out at current densities of 30 and 60 (the values given by Beltzer) and various rates of flow.

With $D_A = 30$ (2·4 amperes) V was 6·5, and with a sufficiently rapid flow the temperature of the anolyte leaving the cell was as low as 2° to 3°. In order that it might not exceed 10° the rate of flow had to be not less than 10 c.c. per minute through the anode compartment, and at $D_A = 60$ correspondingly greater. When all the electrolyte had run through it was passed through a second time without interrupting the current, to obtain the benefit of any rise of the anode potential, the total time being 30 to 50 minutes. Samples of the anolyte leaving the cell were tested immediately, but in no case did 10 c.c. decolourise a single drop of N/20 $KMnO_4$. This is not surprising when one considers the very slow rate of perborate formation, and very small yields obtained, even with the cooled anode apparatus.

In view of these results it is difficult to believe that solid perborate has ever been prepared by means of the Pouzenc cell. It is, however, possible that impurities in the borax used (stated to be "commercial") might give rise to slight oxidizing properties in the solution, e.g. chloride giving rise to hypochlorite. Throughout the present investigation the purest materials were used.

* A solution of double this concentration deposited the solid at this temperature.

SUMMARY.

The previous work on the electrolytic production of perborates has been briefly reviewed and criticised.

Experiments have been carried out in which solutions of alkaline borates of various composition were used as anolyte in suitable electrolytic cells, under various conditions of temperature and current density, a hollow cooled anode being employed in some cases. With dilute and slightly alkaline solutions, such as would be suitable industrially for bleaching purposes, no perborate (or at most a minute trace) was formed in any of the experiments, even with the cooled anode apparatus. Even with much more concentrated solutions only a very small quantity was formed.

It has been shown that an equilibrium is obtained between the rate of formation of the perborate and its decomposition owing to the H_2O_2 formed by its hydrolysis acting as a depolariser, tending to lower the anode potential and being itself destroyed.

Measurements have been carried out of the actual potentials obtained at the anode in certain cases, and of the effect of hydrogen peroxide on the potential. The results accorded well with Grube's theory of overvoltage at a platinum anode and the known electrochemical behaviour of H_2O_2.

Finally, a French patent for the electrochemical manufacture of perborates has been discussed and investigated, a similar apparatus having been constructed on a small scale. It was found to give negative results in practice, no trace of perborate being formed in any of the experiments.

In conclusion the author wishes to express his sincere thanks to Dr. A. J. Allmand, at whose suggestion the above investigation was carried out, for his invaluable assistance and advice.

MUSPRATT LABORATORY,
THE UNIVERSITY, LIVERPOOL,
May, 1914.

THE VAPOUR PRESSURE OF LIQUIDS IN PRESENCE OF GASES.

By F. H. CAMPBELL, M.Sc.

(*A Paper communicated to the* TRANSACTIONS *of the Faraday Society, October*, 1914.)

I. A New Statical Method for the Determination of Vapour Pressures.

While methods for the measurement of the freezing-point, conductivity, viscosity, etc., of solutions have reached a high degree of accuracy and convenience, none of those proposed for the determination of vapour pressure has come into general use.

Beckmann has recently found it necessary to introduce a number of alterations in his well-known boiling-point method,* with a view, among other things, of eliminating the disturbing influence of alterations in the barometric pressure during the course of an experiment. It does not appear, however, that the increased complexity of the apparatus is compensated for by greater accuracy in the results.

With mixtures of two volatile liquids satisfactory results have been obtained by determining the composition of the distillate from a mixture of known composition, at known temperature and pressure.

Von Zawidzki † and Wrewsky ‡ worked at constant temperature, Rosanoff and Easly § at constant pressure. In all cases the experimental difficulties are considerable.

Regnault ‖ determined the vapour pressure of water by saturating a known volume of air by passing it through wet sponge and moist silk screens, absorbing the water in sulphuric acid and weighing it. Results for pure water in substantial agreement with those obtained by the barometric and boiling-point methods have been obtained by various methods depending upon the same principle.

Perman ¶ bubbled air through a series of large Liebig's bulbs, the last being provided with a manometer. Together with Price, Perman has extended the use of this method to solutions.**

Lincoln and Klein †† and Krauskopf ‡‡ passed air over the surface of water, or aqueous solutions contained in a large tube, which was kept in violent lateral motion.

Derby, Daniels, and Gutsche §§ saturated air by passing it through bulbs filled with beads, agitation being effected by rotating the apparatus.

Linebarger ‖‖ employed Liebig's bulbs and liquids other than water. His results were not concordant.

* *Zeit. phys. Chem.*, 1912, 78, 725; 79, 565.
† Ibid., 1900, 35, 129.
‡ Ibid., 1912, 81, 1.
§ Ibid., 1909, 68, 641.
‖ *Ann. chim. phys.*, 1845 (3), 15, 129.
¶ *Proc. Roy. Soc.*, 1903, 72, 72.
** *Trans. Farad. Soc.*, 1912, 8, 1.
†† *J. Phys. Chem.*, 1907, 11, 318.
‡‡ Ibid., 1910, 14, 489.
§§ *J. Chem. Soc.*, 1914, 30, 793.
‖‖ *J. Am. Chem. Soc.*, 1895, 17, 615; *Chem. News*, 1895, 72, 107.

Walker,* on the suggestion of Ostwald, bubbled air through the aqueous solutions under examination and through pure water, the vapour pressure of the former being calculated from the loss in weight of solution and solvent respectively.

The Earl of Berkeley and Hartley † conclude that among the reasons for the failure of Walker's method to give satisfactory results were the facts that the hydrostatic pressure in the several vessels varied, so rendering complete saturation of the air impossible, and that liquid was carried mechanically from solution to pure solvent (water). They eliminated both sources of error by passing the air over the surface of the liquid. A serious disadvantage of the method is that a determination occupies several days.

Will and Bredig ‡ and Orndorff and Carrell § used Walker's original method with ethyl alcohol as solvent, but the method does not seem suitable for use with this liquid, and Will and Bredig found it to be even less so with ether.

Dieterici ‖ employed a differential method, the vapour pressure of a number of aqueous solutions having been determined by the measurement of the movement of a flexible metallic septum, which was compared with that produced by the pressure of the vapour of pure water under the same conditions. Dieterici obtained good results, but the apparatus is complicated and the manipulation difficult.

Lescœur ¶ proposed a method whereby the vapour pressure of a solution is calculated from an observation of the temperature at which a dew forms upon a metallic cylinder in contact with the vapour. The method has been modified and improved by Cumming.** While apparently suitable for use with aqueous solutions, this method is unlikely to be equally so in cases in which organic solvents are employed.

The ordinary static, or barometer, method has not been used with solutions since Raoult †† completed his classic research upon ethereal solutions. The neglect of this apparently simple method is due to the difficulty of obtaining a mixture of known composition in a gas-free condition, and because of the mechanical difficulties in securing efficient stirring.

The investigation of the vapour pressures of binary mixtures of liquids has been confined almost exclusively to those cases in which both constituents are volatile. It was desired to examine the effect of admixing a liquid not measurably volatile at the temperature of experiment upon the vapour pressure of a freely volatile liquid. Since none of the methods hitherto proposed is easily applicable to such cases, that described below was devised.

The principle of the method is that of allowing a liquid, previously saturated with hydrogen at a definite temperature and pressure, to evaporate into a space containing the same gas, under the same conditions. A method based on this principle is no more complicated than the barometric, and is free from the sources of error of that method.

The arrangement of the measuring instrument is shown in Fig. 1. It consists of a glass tube A, open at the bottom, to which are joined a side-tube B, and the tube E, which is bent parallel to A. E is provided with two bulbs, between which a blue-glass point is sealed. The lower end of E is bent at a right angle, and the manometer tube D, graduated in millimetres, is sealed to it parallel to A and E. The levelling tube G,

* *Zeit. phys. Chem.*, 1888, 2, 602.
† *Proc. Roy. Soc.*, A, 77, 156.
‡ *Ber.*, 1889, 22, 1084.
§ *J. Phys. Chem.*, 1897, 1, 753.
‖ *Wied. Ann.*, 1893, 50, 47.
¶ *Ann. chim. phys.*, 1889 (6), 16, 378.
** *J. Chem. Soc.*, 1909, 95, 1772.
†† *Zeit. phys. Chem.*, 1888, 2, 353, and *Ann. chim. phys.*, 1890 (6), 20, 297.

consisting of thick-walled rubber tubing and a glass funnel, is connected to the horizontal portion of E. The end of A is closed by a rubber bung, through which passes the tube C containing the liquid under investigation. The rubber stopper is protected by a layer of mercury.

Fig. 2 is a diagram of the apparatus in which the pure liquid or mixture is saturated with hydrogen. It consists of a tube F, to the bottom of which is sealed a narrow tube with a tap H, and with a similar tube G sealed to the side. F is closed when necessary by a ground-glass stopper, through which is sealed a narrow tube C, the ends of which are capillary.

Method of Experiment.—In the case of a pure liquid a convenient quantity is placed in F, the bottle is put into a bath maintained at the temperature at which the vapour pressure is to be measured, and a slow stream of pure, dry

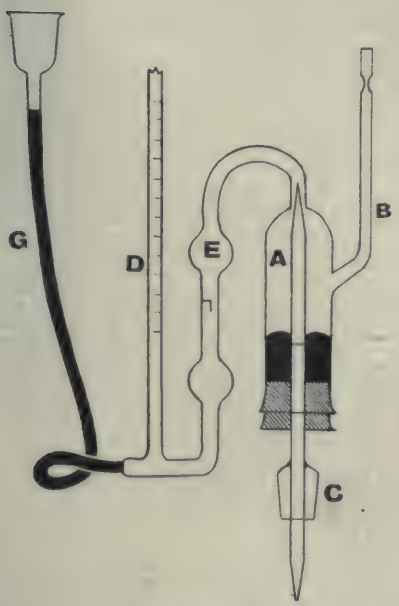


FIG. 1.

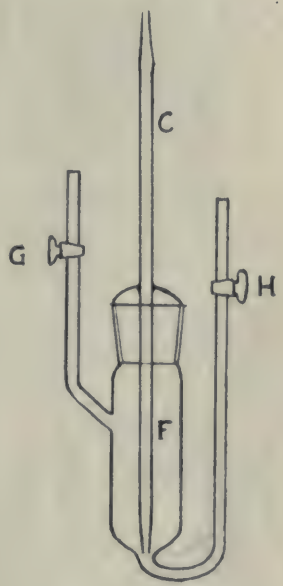


FIG. 2.

hydrogen is passed in through H and out through G. When the liquid is saturated with the gas, the tap on G is closed and that on H manipulated so that the liquid rises slowly in C ; when it is almost full C is sealed at the upper end, removed from F and sealed at the other end. With mixtures the procedure is the same, except that the apparatus is first filled with hydrogen, the upper end of C sealed and the apparatus weighed ; C is removed, a quantity of the non-volatile constituent run in, generally from a graduated pipette, C is replaced, hydrogen is again passed through and the apparatus weighed ; after introduction of the volatile liquid and saturation of the mixture, the apparatus is again weighed. Finally the mixture is brought back to the experimental temperature, the end of C is broken off, and the mixture is introduced and sealed into it as described above.

A measurement is made as follows : The end of C is pushed through the hole in the rubber stopper, deeply scratched about 2 cm. above the stopper, which is then firmly inserted into the open end of A. Pure dry mercury is

poured in through G, and a quantity, sufficient to fill it to a mark etched on the side, is introduced into A. The apparatus is placed in the bath, clamped so that the whole of it except the end of B is immersed, and G is adjusted so that a globule of mercury remains in the horizontal part of E. The air is displaced by passing hydrogen in through B and out through D, the globule of mercury acting as a valve preventing back-diffusion of air. More mercury is now introduced, until its surface is a few millimetres below the blue-glass point, the hydrogen stream is stopped and the end of B is sealed off. The apparatus is now lowered until B is wholly immersed, and, when the temperature of the bath has been reached, the level of the mercury is adjusted until the point just touches its surface ; the mercury level in the manometer is read to 0·1 mm. and mercury is again added through G, generally until the upper bulb in E is partially filled ; the liquid is introduced into A by breaking C at the scratch by gentle lateral pressure and displacing it by mercury, which is effected by careful shaking. In order to promote saturation of the hydrogen the shaking is repeated periodically, the volume being kept constant by addition of mercury through G. When no change in the pressure exerted occurs after agitation, the new level of the mercury in D is read, the

TABLE I.

Liquid.	Temp. °C.	Pressure in		Difference per Cent.
		Hydrogen.	Pure Vapour.	
		mm.	mm.	
Ether	20·0	432·3	442·4	2·28
Ether	30·0	642·1	647·9	0·89
Carbon disulphide ...	30·0	431·9	434·6	0·61
Acetone	30·0	275·8	281·0	1·85
Methyl alcohol ...	40·0	257·4	260·0	0·77
Ethyl alcohol ...	60·0	347·3	350·2	0·82
Water	70·0	230·8	233·8	1·28

vapour pressure being given by the difference between the final and initial readings, corrected to 0° C. for the expansion of mercury and the glass scale. The bath used had a capacity of about 32 litres ; its temperature was maintained within $\pm$ ·02° by means of a toluene regulator with a large bulb ; two opposite sides were of plate-glass. Readings were facilitated by illuminating it from behind.

The thermometers used were graduated to 0·1°, and were standard instruments from Kew Observatory, or had been recently compared with the standards.

Before being used with mixtures the method was tested by determinations of the vapour pressures of a number of carefully purified liquids. Details of the methods of purification are given. The boiling-points, determined with the usual precautions, are recalculated to 760 mm. pressure.

Ether.—Merck's pure ether was washed with ten successive small quantities of water, and allowed to stand over fused calcium chloride, phosphorus pentoxide, and metallic sodium and sodium amalgam in turn. It was kept in the dark in contact with the last-named substances and was distilled as required. It boiled at 34·6°.

Methyl Alcohol.—A pure sample from Kahlbaum was boiled for several hours with metallic calcium under a reflux condenser and was fractionated from it. Moisture was carefully excluded throughout. The fraction used boiled at 65°.

Ethyl Alcohol.—Kahlbaum's 99·8 per cent. alcohol was treated in the same way as the methyl alcohol. It boiled at 78·5°.

Carbon Disulphide.—Merck's "guaranteed pure" material was shaken with copper sulphate solution, dried over fused calcium chloride and fractionated. It boiled constantly at 46·3°.

Acetone.—Crude acetone was fractionated; the portion boiling below 63° was treated with powdered potassium permanganate in the cold, then with ferrous sulphate, and finally with fused calcium chloride. It was twice fractionated; the sample used came over between 56° and 56·15°. It was probably not quite pure.

Water.—Ordinary distilled water was acidified with sulphuric acid and redistilled.

In Table I are given the mean values of several successive experiments with each liquid; in the fourth column are given what appear to be the most reliable of the values obtained by other observers. It will be seen that the differences are small, and that the method is sufficiently accurate for most purposes, including that for which it was devised.

With a mixture a determination can be completed within two and a half hours, with a pure liquid in rather less than half that time. If two sets of apparatus be used, four experiments can be carried out in one day; the method is therefore reasonably rapid.

Substances under examination come into contact with glass, mercury, and hydrogen only, so that the method may be applied to a very large number of liquids. The temperature range also is considerable; any temperature below that at which rubber softens may be used.

II. The Influence of the Nature of the Gas upon the Partial Pressure of the Liquid evaporating into it.

Nernst* states that "if we bring a simple liquid into a vacuum, evaporation takes place, till the pressure of the gas formed has reached a definite maximal value, namely, the corresponding vapour pressure. In presence of another, but an indifferent gas, evaporation takes place till the partial pressure of the resulting vapour is equal to the vapour pressure." It does not appear to be generally recognized that this statement is an inexact assumption; that this is the case, however, is shown by the author's experiments and by the results of all previous investigations carried out under comparable conditions.

In preliminary experiments with the method described, various liquids were allowed to evaporate into air. The results, though concordant, were invariably lower than those obtained by other methods. The air was replaced by a more soluble gas, carbon dioxide, and by a less soluble one, hydrogen. The results of the three series tabulated below show that, in the case of each liquid, the magnitude of the deviation from the most reliable values is greatest in carbon dioxide and least in hydrogen. That the total lowering is not due to the solution of the gas in the liquid is evident; this is clear from a calculation from data given by Just.† Just found the ratio of the concentration of

* *Theoretical Chemistry*, 3rd ed., 1911, 56.
† *Zeit. phys. Chem.*, 1901, 37, 342.

hydrogen dissolved in ethyl alcohol at 25° to that of gaseous hydrogen at 760 mm. to be 0·089 ; it follows that the dissolved hydrogen is present in quantity sufficient to lower the vapour pressure of the alcohol by 0·05 mm., or about 0·08 per cent. ; the lowering actually observed at 60° is 2·9 mm., or 0·82 per cent.

TABLE II.

Liquid.	Temp. °C.	Vapour Pressure in Presence of					
		CO_2.	Air.	H_2.	Pure Vapour of Liquid.		
		mm.	mm.	mm.	mm.	mm.	mm.
Ether	20·0	—	—	432·3	432·8 (*a*)	441·4	442·4 (*b*)
Ether	30·0	550	605	642·1	634·8 (*a*)	647·9 (*b*)	648·2 (*c*)
Carbon disulphide	30·0	402	425	431·9	432·8 (*c*)	434·6 (*a*, *b*)	437·0 (*b*)
Acetone	30·0	—	—	275·8	281·0 (*a*)	—	—
Chloroform ...	30·0	169	238	243·6	(N_2)	247·5 (*a*)	245·9 (*b*)
Methyl alcohol ...	40·0	191	250·5	257·4	243·5 (*a*)	259·4 (*d*)	260·5 (*b*)
Ethyl alcohol ...	60·0	—	344·3	347·3	350·2 (*a*, *b*)	352·1 (*e*)	—
Water	70·0	—	225·8	230·8	233·8 (*a*)	—	—

The values given in the last three columns, for the sake of comparison, are taken from Landolt-Börnstein-Meyerhoffer's *Tabellen* and Castell Evans' *Physico-Chemical Tables.* They are compiled from results obtained by (*a*) Regnault (*Mém. de l'Acad.*, 1862, **26**, 339) ; (*b*) Ramsay and Young (*Phil. Trans.*, 1886, **177**, 1, 123 and 1887, **178**, A., 57) ; (*c*) Battelli ; (*d*) Dittmar and Fawsitt (*Edin. Trans.*, 1886–87, 23, II, 509) ; (*e*) Schmidt (*Zeit. Phys. Chem.*, 1891, 8, 628).

No value for chloroform in hydrogen is given, very irregular results having been obtained. It is supposed that hydrogen reacts with chloroform, an hypothesis first put forward by Just* to account for his inability to establish equilibrium between hydrogen dissolved in chloroform and the gas. Nitrogen appears to be completely indifferent ; the result in presence of this gas is 0·94 below that of Ramsay and Young. Since carbon dioxide probably forms additive compounds with ether, chloroform and the alcohols,† even at the comparatively high temperatures employed, the great effect of this gas upon the vapour pressures of these liquids was to be expected.

It might be thought that the deviations noted are due to some undiscovered source of error peculiar to the method used ; a review of other work done under comparable conditions, however, makes it evident that this is improbable.

From the present point of view the most important work is that carried out by Regnault.‡ Having found that the pressures calculated from the weights of water in known volumes of saturated air and nitrogen respectively were invariably from 1 to 2 per cent. lower than those developed *in vacuo*, Regnault extended the investigation to other liquids. In addition to that already referred to, Regnault employed two statical methods.

The first of these was similar in principle to that used by the author, a small bulb containing the liquid being broken in a flask of 600 to 700 c.c.

* Loc. cit.

† Cf. Hempel and Seidel, *Ber.*, 1898, 31, 2907. Dolezalek, *Zeit. phys. Chem.*, 1910, 71, 191.

‡ *Ann. phys. chim.*, 1845 (3), 15, 129, and *Mem. Acad. Sc.*, 1862, 26, 679.

capacity to which a mercury manometer was attached. In all cases the gas present was air, the liquids were ether, carbon disulphide and benzene. The conditions were varied in several ways, but low results were always obtained; with ether the differences varied between 1 and 2·9 per cent., with carbon disulphide between 0·8 and 1·2 per cent., while with benzene the limits were 2·9 and 4·8 per cent. No reliable data as to the solubility of gases in ether are available, but it is of interest to note that benzene is a much better solvent for gases than is carbon disulphide.

In the second series of experiments small quantities of ether were introduced into a graduated tube containing air, hydrogen, or carbon dioxide. The gas pressure corresponding to each volume being known at a constant temperature, a measurement of the total pressure after each successive decrease of volume gave the partial pressure of the ether vapour. It was found that when the gas pressure was approximately atmospheric, that of ether was 1·3 per cent. too low in air and 1·5 per cent. too low in hydrogen, but that, at about 1,200 mm. gas pressure, the pressure of the ether vapour slightly exceeded that developed *in vacuo*. Certain of the results obtained in carbon dioxide are given in Table III.

TABLE III.

Temperature.	Partial Pressures.		Differences.
°C.	CO_2.	Ether.	Per Cent.
	mm.	mm.	
7·7	0·00	260·0	—
,,	535·38	234·40	9·8
,,	740·38	245·80	6·2
,,	1,165·78	235·43	9·4

In his dynamical experiments the gas used by Regnault was air; he confirmed his previous results with water, found that alcohol gave very low results, and that the values found with ether were in good agreement with those calculated.

Comparatively recently Shaw* repeated Regnault's experiments with water, using his original dynamical method. Like Regnault's, Shaw's results were slightly low.

Tammann† modified Regnault's method slightly and applied it to the determination of the vapour pressures of water, unsaturated and saturated aqueous solutions, and of hydrated salts. All the experiments were done at temperatures very near 35°. The mean value for pure water was somewhat lower than Regnault's; unsaturated solutions gave irregular results, owing no doubt to the fact that they were not stirred; with saturated solutions and hydrated salts the relative vapour pressures were higher than those measured in other ways.

It is suggested that this last fact is due to a diminution in the vapour pressure of water in air, not shown by saturated solutions and hydrated salts, or shown to a much smaller extent. That this explanation is probably correct is shown by the excellent agreement between the values given by Frowein‡ and others and those of Tammann when the values given by

* *Phil. Trans.*, A., 1888, 179, 73. † *Wied. Ann.*, 1888, 23, 322.
‡ *Zeit. phys. Chem.*, 1887, 1, 1.

the latter are recalculated, the pressure developed by water *in vacuo* being substituted for that determined by him.

Justification for the assumption that a saturated solution of sodium chloride develops the same pressure in air and *in vacuo* is found in the observation of Geffcken* that the solubility of oxygen in sodium chloride solutions at 25° falls off rapidly with increasing concentration of the salt, so that it is approximately one-half that in pure water at a concentration of about 10·5 grams per 100 c.c.; hence it may be taken that the solubility of oxygen and nitrogen at 35° in a saturated solution, containing approximately 35 grams per 100 c.c., is negligibly small. If P_A be the vapour pressure of pure water, as determined by Tammann, P'_A that of the sodium chloride solution under the same conditions, and P_v that of pure water *in vacuo*, we find that $\frac{P'_A}{P_A} = 0{\cdot}769$, or about 5 per cent. too high, but that, taking 41·85 mm. as the value for P_v, $\frac{P'_A}{P_v} = 0{\cdot}732$, 4·8 per cent. lower.

It may be assumed that the solubility of gases in the water of crystallization of hydrated salts is negligible, so that the same considerations apply as in the case of saturated solutions. Tammann seems to have failed to realize that the air was not passed over any of the salts at a rate sufficiently slow to allow of its saturation, except in those cases in which the vapour pressure is relatively high. A consideration of the cases in which the relative vapour pressure is independent of the rate at which the air was passed shows that the agreement between Tammann's results and those of Frowein is very close when P_v is substituted for P_A. P'_v is the vapour pressure of the salt *in vacuo*.

TABLE IV.

Salt.	$\frac{P'_v}{P_v}$. I.	$\frac{P'_A}{P_A}$. II.	$\frac{P'_A}{P'_v}$. III.	Differences II–I.	Differences III–I.
$Na_2HPO_4 \cdot 12H_2O$	0·879	0·918	0·886	0·039	0·007
$ZnSO_4 \cdot 7H_2O$	0·730	0·774	0·739	0·044	0·009
$MgSO_4 \cdot 7H_2O$	0·594	0·622	0·595	0·028	0·001

Linebarger† applied a modification of Regnault's method to the determination of the vapour pressures of mixtures of volatile liquids and incidentally measured those of a number of them in the pure state. In all cases in which the probable experimental error is small enough relatively to be neglected, Linebarger's results are somewhat lower than those obtained by other observers. These differences are attributed by him to the volatility of the liquids, but it will be seen that the differences increase with the solvent power of the liquids for gases‡ and not with the volatility.

With the exceptions to be mentioned immediately, the above review includes mention of all the work of this kind hitherto published. It is, in consequence, of importance that the results deviate, in all cases, in the same direction from those obtained by methods involving the use of gas-free liquids, that is, that they are always low. The exceptional results referred

* *Zeit. phys. Chem.*, 1904, 49, 257. † Loc. cit.
‡ Cf Just, loc. cit.

to are those for water, obtained by Perman, Krauskopf, and Derby, Daniels and Gutsche, whose papers have been cited.

It has generally been assumed that failure to get satisfactory results of vapour pressure measurements in presence of a gas, almost always air, has been due to experimental error, and, in cases in which a stream of gas was used, to incomplete saturation. Regnault convinced himself that the differences which he found were due to actual differences of pressure. He suggested that the molecular attraction between the substance of the walls and the vapour particles causes condensation and that equilibrium is never reached, because the rate of evaporation of liquids in presence of gases is slow and because a film of liquid of the thickness requisite to saturate the walls cannot form on account of the force of gravitation.

TABLE V.

Liquid.	Temp. °C.	Vapour Pressure.		Difference per Cent.
		Linebarger.	Other Observers.	
		mm.	mm.	
Carbon disulphide ...	20·0	296·4	298·1	0·57
Benzene	34·8	145·4	147·2	1·22
Chloroform	35·0	290·1	301·1	3·65

It is suggested that an explanation more in consonance with the facts recorded in this paper is that gases form films on the surfaces of liquids, as on those of solids; in other words, that liquids, like solids, adsorb gases. It is known that, of the three gases, carbon dioxide, oxygen and hydrogen, that nearest to its critical temperature under ordinary conditions—carbon dioxide—is the most freely soluble and is adsorbed to the greatest extent by solids, notably by charcoal, and that hydrogen, the farthest removed from its critical temperature, is least soluble and least easily adsorbed by charcoal. The order is the same when we arrange the gases according to the magnitude of the vapour pressure lowering which they cause. This parallelism lends weight to the hypothesis of the existence of a highly concentrated film of gas at the surface of a liquid, and further, certain of Regnault's observations receive satisfactory explanation upon this assumption.

In his first series of statical experiments Regnault found that the greatest pressure at any particular temperature was developed immediately after the mixture of gas and vapour had been raised to that temperature, and that the maximum pressure was greater when the alteration in temperature took place quickly; in all cases, however, a gradual fall followed. In the second series the highest vapour pressure at any particular partial pressure of gas was developed immediately after a reduction in volume; as before, a gradual fall followed. It is evident that, in either case, a fresh film of liquid must be formed, which exerts a pressure equal to or approaching that developed *in vacuo*, and that on standing gas is adsorbed and the pressure falls in consequence.

In reference to the results obtained by Krauskopf and others, it is noteworthy that they resorted to violent agitation of the liquid, while Regnault and Tammann passed the gas over the surface of the unstirred liquid. It

would seem that the success of the former was due to the prevention of the formation of a gas film on the liquid surface, not, as they seem to imply, solely to having saturated the gas.

The hypothesis does not account equally well for the fact that Regnault found that ether in air and hydrogen gave the lowest partial pressures at the lowest total pressures and that it increased with the latter until, when the gas pressure was approximately 1·5 atmospheres, that of ether was very nearly the same as *in vacuo*. It is almost certain that at the low pressures the amount of liquid ether was so small that there was no true free surface. Were this the case the difficulty largely disappears, for it has been proved that, even *in vacuo*, thin liquid films exert a lower pressure than the normal.

The somewhat peculiar results obtained with ether in carbon dioxide are explicable upon the above assumption and that of the formation of a compound of ether and carbon dioxide. Thus, with increasing pressure of the gas the amount of liquid ether increases, and with it the partial pressure, but, before a true liquid surface has been formed, the increasing concentration of the additive compound has become the chief determining factor and the partial pressure of the ether again falls as the total pressure increases.

The matter, which is of importance from the point of view of the determination of the solubilities of gases in liquids and in other ways, is being investigated further in this laboratory.

Summary.

1. A statical method for the measurement of the vapour pressures of pure and mixed liquids over a considerable range of temperature, involving the use of a very simple form of apparatus, has been devised.

2. The results of measurements of the vapour pressures of a number of pure liquids are recorded, which prove the method to be capable of yielding results in good agreement with those generally accepted as standard.

3. It has been proved by experiments carried out in a number of ways, by the author and others, that liquids exert a lower vapour pressure in presence of gases than when in contact with their own saturated vapours only.

4. It has been shown that, in the case of any one liquid, the lowering is greater the more soluble the gas ; certain evidence has been adduced which indicates that, with any one gas, the lowering is related to the solvent power of the liquid.

5. It is pointed out that in all cases the amount of gas dissolved is quite insufficient to account for the whole of the observed lowering and that the differences tend to disappear when the liquid is violently agitated.

6. It is suggested that the concentration of a gas in an unstirred liquid is much greater at the surface than in those parts of the liquid removed from the influence of the forces there operative.

This investigation was undertaken at the suggestion of Professor Orme Masson, and the author has great pleasure in acknowledging his continued interest and, especially, his suggestion of the above-mentioned hypothesis.

The University of Melbourne.

THE HARDENING OF METALS.

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Monday, November 23, 1914, at the Chemical Society, Burlington House, London, W., a **General Discussion** on **The Hardening of Metals** took place. **Sir Robert Hadfield, F.R.S., President,** was in the chair.

OPENING ADDRESS

By SIR ROBERT HADFIELD.

The Proceedings were opened by the **Chairman,** who delivered the following Address.

In opening the discussion on this interesting topic, "The Hardening of Metals," I might perhaps add a few words as to why this subject comes to be discussed here to-night.

At the last meeting of the Iron and Steel Institute several valuable papers were presented, but some of these were not so fully discussed as their importance warranted. As all of us know, at the General Meeting of such an Institute, when so much ground has to be covered at one meeting, it is sometimes not then possible to do justice to the subjects brought up for consideration.

It was suggested, therefore, that without in any way interfering with the work of the Iron and Steel Institute, there would be no objection to our Faraday Society offering facilities for a further and fuller discussion of some of the papers then dealt with, and also further papers relating to the hardening of steel. Such a proposal met with no objections, and so here we are to-night, when I trust an opportunity will be given to each of those present wishing to take part in the discussion and to put forward their views. The topic is such a wide one that I much fear one evening will leave but scant opportunity to do justice to the important subjects which concern all of us.

Before steel was introduced, except the handful produced by the crucible or puddling process, the main object of the metallurgist was to keep his metal as soft as possible. The reason for this was that in those days, when heat treatment was practically unknown, an approach to hardness meant brittleness, and, therefore, the material was useless.

Imagine a wrought iron of hardened or stiffened nature, that is, in some way stiffened up or even case hardened ; a material so produced would have been of little or no value. Let me here add, it must not be concluded that this term " hardened " always infers the glass-scratching hardness of quenched steel containing high percentages of carbon.

As, however, events began to march rapidly, the user soon found himself on the horns of a dilemma. For example, as railroads began to be introduced, rails were demanded which would not wear out so quickly, and tyres which would not need renewing every few months. In the very nature of things, a new type of material therefore became necessary. It was almost entirely for this reason and cause that modern steel appeared on the scene, and thereby came the introduction of processes which enabled material to be produced which can be truly termed " of hardened character," that is, hardened by the introduction of carbon as compared with wrought iron in which carbon was practically absent ; in other words, modern steel was invented. Just imagine that but little more than fifty years ago there was practically no steel in existence of the grades used on the present enormous scale.

When Bessemer's process was first sprung upon an astonished world in the year 1863, and soon afterwards followed by the great Frenchman, Martin, to whom the Iron and Steel Institute has just awarded the Bessemer Gold Medal, with his open hearth or regenerative furnace, it was at once seen that a new era had opened, and thus commenced that marvellous progress first of all on railroads in which rails of what may be truly termed " the hardened metal steel " were used, shortly afterwards followed by applications in many other directions. Since that time railroads have opened up this great world of ours, and from this development has sprung every other conceivable one, chiefly helped on by the metallurgist, who has risen to such new requirements. It was but yesterday, that is, until this unhappy war broke out, we had a world in which the enormous quantity of some 55,000,000 tons of steel, or what may be termed " hardened " metal, was being used annually and put into service for one purpose or another. Let it be here remarked that the greater the expansion in the use of steel the greater has become the hardness of that metal. There is, of course, still an enormous quantity of material used of mild quality, but except to a very small degree even most of that is much harder than the old wrought iron.

The Brinell ball hardness number of wrought iron is certainly under 100, whereas we are now getting up to special steels with no less than 300 Brinell ball hardness number. Yet these special steels can be used with even greater safety than wrought iron, that is, steels which are able to resist severe vibratory stresses, sudden shocks, wear and tear, and all this in a manner which the toughest and softest wrought iron would not fulfil. As can be imagined, it has required the efforts of many minds to arrive at this position of great advance, much of this progress having taken place as a result of the development of alloys of iron with other elements. Practically the first paper on this subject was that which I read in 1887 in connection with my discovery of alloys of iron and manganese known as manganese steel, followed by papers on alloys of iron with silicon, aluminium, nickel, chromium, tungsten, and other elements.

It will, therefore, be seen that it may be very truly said the world's future progress literally depends upon understanding correctly and in

a scientific manner "The Hardening of Metals," a subject to which we are going to give our attention this evening.

If we can, therefore, add but a little to our knowledge of this fascinating and important subject, we shall indeed be doing good work at home and abroad.

Whilst we are to-night going to discuss more particularly the *rationale* of hardening, the reasons why and wherefore rather than practical applications, if we can understand the former, then advantages will be obtained in the latter, for this must as surely take place as night follows the day.

We have present with us this evening an authority on this subject, Dr. Beilby, whose fascinating studies on "The Amorphous Theory of the Hardened State" entitle his opinion to special consideration, and we shall be most delighted to hear him. Dr. Beilby's theories are now generally accepted for the hardening of metals by cold working. To quote his own words, "Mechanical deformation produced smaller crystalline grains, and the increased hardness is due to the crystalline fineness of structure."

We are also to have papers by Professor C. A. Edwards on "The Hardening of Metals by Quenching"; Mr. McCance on "The Interstrain Theory of Hardening"; Mr. Humfrey on "The Part Played by the Amorphous Phase in the Hardening of Steels"; Dr. Desch on "The Hardness of Solid Solutions," and "A Note on Twinnings and the Martensitic Structure"; Dr. Martin Lowry and Mr. Parker on "Metallic Filings"; Professor Howe on "Hardening with and without Martensitization," and a communication from Dr. Stead. I would also add that Mr. Heathcote will demonstrate with some apparatus for determining hardness.

This question of accurately determining the hardness of steel alloys has become so important, that the Institution of Mechanical Engineers has now formed a Special Committee known as the Hardness Test Research Committee, which with its able Chairman, Dr. Unwin, is investigating and discussing all the phases of this important and fascinating subject.

In this respect might I also respectfully and with regret refer to the death of the late Dr. Geheimrath Martens, of Gross-Lichterfelde, whose personal kindness to me and many other Englishmen who have visited Berlin cannot be forgotten. It was he who, next to Brinell, Turner, and Shore, helped to originate and develop correct methods of studying the hardness of metals. Although we are, alas, at war with his nation, that does not blind or prevent us from appreciating the merits of our enemy. In the same way as we handed back his sword to Captain von Müller, so, notwithstanding the unhappy state of war existing between these two great nations, England and Germany, officially as your President of this Faraday Society, whose name in itself indicates English admiration and respect for the work of the scientist, we tender our respectful sympathy to the family of Dr. Geheimrath Martens, who added so many interesting contributions to scientific investigations in matters relating to mechanical and other sciences, including the special one relating to the hardness of metals. It will be remembered that the metallographic terms "Martensite" and "Martensitic" were named in honour of Dr. Martens by the renowned French metallurgist, M. Osmond.

Before concluding, I should like to show a specimen of steel of unusual value and interest, bearing as it does upon the title of our subject, "The

Hardening of Metals.'' This specimen, which is illustrated in Plate I, is probably the first to be exhibited in modern times of an ancient piece of high carbon steel which has been hardened by quenching. The following is the analysis of its composition :—

Carbon.	Si.	S.	P.	Mn.	Cr.	Ni.	Fe.
·70	·04	·008	·020	·02	trace	trace	99·2%

It was possible to obtain a fracture of the specimen, which weighed about 8 oz., was 3 in. in length, $2\frac{1}{2}$ in. in breadth, $\frac{1}{2}$ in. in thickness. This showed fine crystalline but rather brittle structure. After removing the scale the Brinell ball hardness number was found to be 146. On cutting the specimen through with a saw there was found to be a quite fair proportion of the original metal still unoxidized.

I received this specimen a few months ago from the Superintendent of Archæology in Western India, Mr. Bhandarkar. One of the special points is that notwithstanding the large number of specimens of ancient iron and supposed steel I have examined during the last few years, none of them have contained sufficient carbon to be termed steel in our modern time meaning. This specimen, as will be seen from the above analysis, contains as much as ·70 per cent. carbon, which indicates that it can be readily hardened by heating and quenching in water.

In other words, this material has been in its present condition for probably more than two thousand years, and now, after being heated and quenched, hardens exactly as if it had been made only yesterday, thus showing that in this long interval, and beyond surface oxidation, this specimen has undergone no secular change of structure, or alteration in the well-known capacity of an alloy of iron with carbon to become suddenly possessed of glass-scratching hardness after being heated and quenched in water or other cooling medium. The photomicrograph of the material (Plate II) in the original condition '' as received '' shows Pearlitic structure, and consists of elongated and irregularly disposed crystals of sorbitic pearlite upon a ferrite ground mass. The specimen has evidently not been reheated above the Ac_1 point since it was deformed. The crystallization varies from fine to coarse. In places the structure is blurred, as a result probably of mechanical work. The carbon in the specimen appears to vary from ·30 per cent. to ·75 per cent. The area photographed is nearer the low limit. There are seams of slag in certain portions of the specimen, but apart from these the material appears to be of similar type to ordinary modern carbon steel. The structure of the specimen (Plate III) after being quenched from 850° C. in water is Martensitic. Although the specimen was exceedingly small—about 7 mm. by 4 mm.—yet the quenching has not been successful in preventing a small amount of troostitic structure from developing and somewhat destroying the definition of the Martensitic needles by darkening the ground mass. On the edges of the specimen where no troostitic structure develops the specimen will scratch glass.

I therefore show two specimens, one in the original condition as received, the other after having been hardened. As will be seen, after quenching the steel readily scratches glass.

Mr. Bhandarkar assures me there is not the slightest doubt about the antiquity of this specimen from the bars found beneath the stone pillar of Heliodorus at Besnagar, India. The specimen in question was

PLATE I.—Specimen of Ancient Indian Steel (probably B.C. 125).
Full Size.

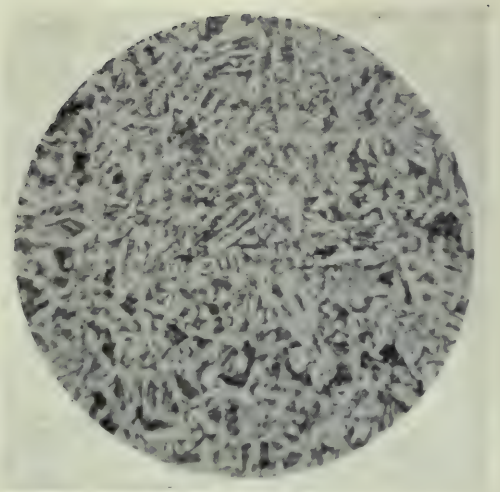


PLATE II.—As received. × 100.

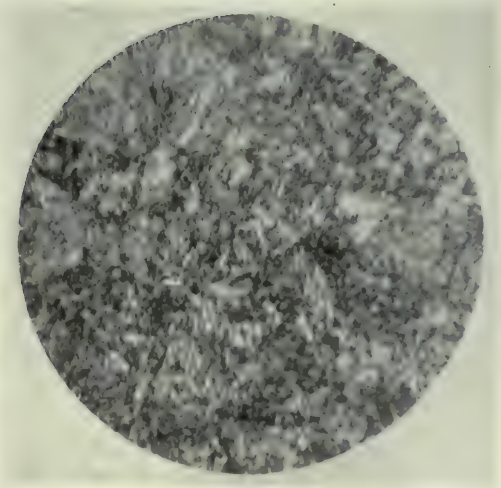


PLATE III.—Quenched from 850° C. × 400.

PLATE IV.—This Column is known as Khan Baba, in Besnagar, in the Bhilsa District, Gwalior State (Central India).

The inscription on this Pillar states: "The Pillar was erected by a Greek called Heliodorus, son of Dion, who was an ambassador dispatched by the Greek king Antialkidas to the court of an Indian Prince named Bhagabhadra, who ruled over Central India." It is believed this enables the date of the erection of the Column to be considered as about 125 B.C. Immediately below the lower end of the Pillar, and between it and the foundation stones, two pieces of iron were found pushed in between the slabs.

found at the bottom of the pillar, shown in Plate IV, and dating back to about 125 B.C. Mr. Marshall, the Director-General of Archæology in India, was present when the base of the column was excavated, and affirms that from all he saw the column could not have been shifted at a later date, or that the bars found could have been subsequently inserted.

The column itself is locally known as Khan Baba. On this is an inscription recording that it was a Garuda-dhvaja erected in honour of the god Vasudeva, that is, in front of his temple. Garuda is more or less a fabulous bird, and is believed by the Hindus to be the vehicle of that god. Garuda-dhvaja means a pillar surmounted by the figure of Garuda, and such pillars are generally put up before temples dedicated to Vasudeva. The inscription shows that the pillar was erected by a Greek called Heliodorus, son of Dion, who was an ambassador despatched by the Greek king Antialkidas, King of Taxila, to the court of an Indian Prince named Bhagabhadra, who ruled over Central India.

It is, therefore, quite possible that the metal of the bars, which Mr. Bhandarkar thinks are in the form of chisels, may have been forged by Greeks. Probably, however, they were really wedges, and were inserted to steady the column, specially as they were found between the base of the column and the first foundation slab. The specimen examined is folded over and thinned out at the edges.

THE HARDENING OF METALS—INTRODUCTORY PAPER.

Dr. G. T. Beilby, F.R.S. (Glasgow), then read the following Paper as an Introduction to the General Discussion.

The subject may be conveniently arranged under the following sections :—

I. Hardening of the pure ductile metals results from any form of cold working.

II. Hardening of the pure ductile metals may result from their mixture with each other or with non-metallic elements, e.g. hydrogen, nitrogen, carbon, etc.

III. When these mixtures are ductile they, like the pure metals, may be further hardened by cold working.

IV. Certain of these mixtures have the property of hardening by chilling.

The sudden drop in temperature which results from chilling may act in two ways :—

(*a*) It may stereotype the form of chemical combination or of structure, crystalline or non-crystalline, which is in the condition of equilibrium at the temperature at which chilling begins.

(*b*) It may set up contraction strains within the cooled mass. These strains may be wholly or in part either within or beyond the elastic limits. When the strains exceed the elastic limit and permanent deformation occurs, then hardening may result as in II.

As a means of throwing light on the molecular structure of solids the study of the phenomena under Section I has appealed to me very strongly, because of certain great advantages which are inherent to this side of the subject. Chief among these advantages is the fact that in a pure metal we have only one kind of chemical or ultimate atom, and that in certain ductile metals the chemical molecule is monatomic. It follows that in dealing with a given mass of metal, either "hard" or "soft," we are dealing with the same number and kind of atoms or molecules occupying practically the same volume in whichever state the aggregate is found. In a problem which is essentially a physical one it is no small advantage to know with certainty that chemical questions have been completely excluded. The ease and certainty with which the pure ductile metals, in particular gold, silver and copper, can be passed from one state to the other—soft to hard, or hard to soft—is an important practical advantage in experimental work. Further, these metals recrystallize from the hardened state at temperatures which are so much above the ordinary atmospheric temperature that their permanence in the hardened state is assured, while the fact that their recrystallizing temperatures are more than 800° below the liquefying point at once removes any suspicion

that the mobility of the atoms or molecules, which is a necessary feature of recrystallization, is of the same degree as the mobility of the liquid molecules.

The problem of the two states in the pure ductile metals can be stated thus :—

A centimetre cube of metal in the hard state containing x ultimate atoms or molecules has certain well-marked physical qualities. This cube when heated to about 300° loses these characteristic qualities, so that from the physical point of view it might be a different metal. It still contains x ultimate atoms or molecules, and the volume they occupy is still practically a centimetre cube. As the number of molecules and the space they occupy are both constant, the *intrinsic cohesive force* of the aggregate is also constant, though the *effective cohesive force*, on which the greater or less rigidity of the aggregate depends, will vary (1) with changing energy conditions, and (2) with the relative positions of the atoms or molecules to each other *if they possess polarity*. With respect to energy changes in passing from one state to the other, it has been conclusively proved that there is a considerable storage of potential energy in the hardened state and that this storage is associated with a marked reduction in the vibrational freedom of the atoms or molecules. We may picture this as due to the molecules being so pressed together that they curtail each other's vibrational freedom. It is not, however, quite correct to speak of their being "pressed" together, seeing that the force which enables them to hold each other more closely is their own attraction or cohesion.

From the first it has appeared to me most probable that the atoms or molecules do possess polarity, either as an intrinsic property or more probably as a property developed by heat vibration, and that the metal in the hard vitreous condition is truly amorphous, inasmuch as its atoms or molecules are crowded together heterogeneously as regards their polarities. The temperature-elasticity curves, as well as the curves of thermoelectric potential, show the existence of distinct stages in the recovery from strain as the annealing temperature is raised. There is a comparatively quick relief when the metal is heated to 100°, followed by a slower rate till the crystallizing range is reached. Over the comparatively short crystallizing range the relief is so rapid that it definitely suggests that a new type of structural change has set in. The microstructure shows that this corresponds with (1) the disappearance of the characteristic hardened structure, (2) the appearance of minute detached crystalline aggregates, and (3) the apportionment of the whole mass among well-developed crystalline grains.

It seems natural to picture the earlier steps in the relief of strain as due to the energizing effect of rising temperature on the molecular vibrations. A slight general expansion of the mass will occur, and the potential energy released by this expansion will augment the kinetic energy of the vibrating molecules, but not to the point at which they can free themselves sufficiently to enable them to take their true orientation under the influence of the crystalline nuclei in the mass, which always persist in spite of the most drastic deformation. When the temperature is raised to the beginning of the crystallizing range we may suppose that a proportion of the molecules have attained the necessary amplitude of vibration to set them free to orient, and with rising temperature further progress towards complete orientation and re-orientation takes place over the remainder of the crystalline range till the whole mass is apportioned into crystal grains, each with its own orientation. *Re-orientation* of the freely vibrating molecules must certainly occur as the larger grains impress their orientation on their smaller neighbours or on other partially oriented aggregates.

In this type of recrystallization at a temperature which may be as much as 800° or 1,000° below the liquefying point, it is not necessary to suppose that there is any transport of molecules from crystal to crystal. Orientation of the molecules only requires that they shall turn *in situ* in response to the cumulative vibration of a more powerful crystal.

The foregoing illustration shows the remarkably self-contained nature of the problems of Class I, as well as their almost elemental simplicity, at least in outline. The qualitative differences between the two states are not disputed. That these are due to the intrinsic properties of the pure metals is proved by the fact that these differences become more sharply defined as metals of greater purity are used. Most of these differences lend themselves to exact measurement, as, for instance, the hardness, rigidity, or mechanical stability, the electrical conductivity, the thermoelectric potential, the energy of solution and the elasticity by the acoustical method. The microstructure can be recorded by photography, though we need to remember that no photographic records, however perfect, can take the place of direct study with the microscope. In every case the thermally stable crystalline state supplies a fixed standard of reference. No uncertainty attends the passage of the pure metal from the hard to the soft fully crystallized state, neither is there any uncertainty in the reverse change from soft to hard by cold working, but the particular mode by which this working is effected, and the extent to which it is carried, mainly affect the ultimate *texture* of the hardened metal and therefore also its mechanical qualities.

This question of *texture* has not received the attention which it deserves, yet it absolutely stares us in the face in the sections of drawn or rolled work. It may be so coarse that it is clearly seen by the unaided eye, or so minute that the highest powers of the microscope are needed to resolve it fully, but whatever the scale of magnitude the texture is always true to its type.

It is the existence of "texture" in cold-worked materials which makes the value of all density determinations of hardened metal so uncertain. If cold working brings some of the molecules so close together that they interfere with each other's freedom of vibration, it is clear that if the volume of the hardened mass is not less than that of the corresponding crystalline mass, other groups of molecules must spread themselves out in wider spacing.

To return to the centimetre cubes of our illustration, we have seen that the difference between the two must be due to some difference in the arrangement of the atoms or molecules in the given space. The greater hardness or rigidity of the hard cube shows unmistakably that the atoms or molecules move over each other with much less facility than they do in the soft cube. There is also an increase of tenacity which points in the same direction, and in addition confirms the suggestion that the cohesion of the atoms or molecules is being used with much greater effect. It must be admitted that these are *facts*, explain them how we may. But there are more facts about the hard cube. The elasticity of its atoms or molecules has been seriously impaired. The acoustical test of elasticity which Mr. McCance has used, and the first use of which in this connection he attributes to M. Robin in 1911, had already been extensively used by me and was described in 1907.* The coincidence of the elasticity curves with the e.m.f. and tenacity curves was also demonstrated and discussed in the same paper. The steps in the release of elastic strain and their correspondence with the course of recrystallization were also demonstrated and discussed. Two sets of facts have therefore been established; the mechanical properties show that the atoms or molecules are holding each other more firmly, while the physical

* *Proc. Roy. Soc.*, A, vol. 79, 1907, p. 475.

tests show that a state of elastic strain exists throughout the aggregate. My interpretation of the facts is that the second set confirm and emphasize the first set in showing that in the molecular structure of the hard cube a proportion of the molecules are either drawn more closely together by their intrinsic cohesion or are turned into positions relatively to each other in which their mutual cohesion can come into more favourable action.

Having traced the passage from hard to soft as recrystallization sets in and completes itself over a certain range of temperature, let us now try to follow the reverse operation. If we drop a hammer on the soft cube the change is accomplished at a blow, and no method has yet been devised by which the steps which separate the soft from the hard state can be watched as they occur. The amorphous theory for which I am responsible is that under mechanical disturbance crystalline lamellæ or sheets break down momentarily into the liquid state and instantly resolidify in a vitreous amorphous condition, thereby forming a hard cementing material which binds the disturbed and partially broken-up crystal aggregates together. By carrying out experimental observations on surface flow in metals and other solids it appeared to me that conclusive evidence had been obtained that the intermediate liquid state is a necessary and invariable step in the breaking down of the crystal structure by flow. It further appeared that the type of internal structure, the "texture" of cold-worked metals, strongly confirmed the view that the new aggregate shows all the indications of being a concreted mass. This view, that there is an actual liquefaction and resolidification, appears to account in a satisfactory way for the vitreous character of the flowed metal, for it is really the product of a liquid which has been solidified with a rapidity far exceeding that which can be reached by the chilling methods with which we are familiar. This instantaneous cooling is, of course, accompanied by equally sudden contraction, with its accompanying state of elastic strain.

It has appeared best that my remarks should be confined to Section I of the division of the subject with which this paper begins. A study of recent papers on hardening has satisfied me that several able workers in the other sections of this field have not quite realized the significance of the well ascertained facts in Section I. My aim has therefore been to draw attention to the significance of these facts.

THE INFLUENCE OF ALLOTROPY ON THE METASTABILITY OF METALS, AND ITS BEARING ON CHEMISTRY, PHYSICS, AND TECHNICS.

Professor Ernst Cohen (Utrecht) was to have read the following Paper on "The Influence of Allotropy on the Metastability of Metals, and its bearing on Chemistry, Physics, and Technics," but as at the last moment he was unable to come over from Utrecht, the Paper was taken as read. Professor Cohen cabled his greetings to the meeting, and said he hoped to visit the Society at a later date.

1. It might seem surprising that a man is invited to take part in a discussion on the hardening of metals who never before occupied himself with this important part of metallography. However, I think the Council of the Faraday Society has seen clearly in giving its members the opportunity of becoming acquainted with a number of phenomena unknown up to the present, and which will, in my opinion, modify our conceptions about metals very markedly.

My first duty is to thank the Council for inviting me to give here a survey of the investigations I have carried out these last few years on the metastability of metals in collaboration with my pupils, Messrs. Helderman, Moesveld, van den Bosch, de Bruin and Dr. S. Wolff.

2. One of the starting-points of our work was suggested by the following clauses set forth in a paper by Matthiessen and von Bose,* "On the Influence of Temperature on the Electric Conducting Power of Metals": "Pure cadmium, when heated to about 80°, becomes exceedingly brittle; in fact, it may be powdered in a hot mortar with great ease. We should not have been able to carry out the determinations if the wires had not been varnished, as the movement of the oil by the stirrer would have caused them to fall to pieces. . . ."

3. From these and other remarks in the paper mentioned we got the impression that we were dealing with allotropic transformations of the metals which had not been observed before. Up to the present we have occupied ourselves with bismuth, cadmium, copper, zinc, antimony, sodium, potassium and lead. As it is impossible to treat the subject here in full, I intend giving a description of the methods by which the general results were obtained, choosing cadmium and lead as examples, these being especially instructive. As for the other metals concerned, I must refer to our papers in the *Proceedings of the Koninklijke Akademie van Wetenschappen te Amsterdam* † and the *Zeitschrift für physikalische Chemie.*‡

4. Before mentioning the methods used, it may be pointed out that the metals experimented with were of a high degree of purity.

Our cadmium (Kahlbaum, Berlin) contained 0·005 per cent. of lead, 0·001 per cent. of iron, and a trace of zinc, whilst the impurities of our lead

* *Phil. Trans.*, **152**, 1 (1862).
† *Proceedings*, **16**, 485, 565, 628, 632, 807 (1913–14); **17**, 54, 59, 60, 122, 200 (1914).
‡ *Zeitschr. f. physik. Chemie*, **85**, 419 (1913); **87**, 409, 419, 426, 431 (1914).

(Kahlbaum, Berlin) were 0·001 per cent. of copper and 0·0006 per cent. of iron.

5. The investigation was carried out using the pycnometer, the dilatometer, and also the electric potential method.

1. *Experiments with the Pycnometer.*

6. Our experiments on bismuth had proved that metals may show very great retardation in undergoing molecular changes at temperatures either above or below their transition-points. This reluctance to undergo change is doubtless one of the reasons why the phenomena to be described here remained undiscovered until so late a period.

7. We generally used the pycnometer (Fig. 1) described by Johnston and Adams* (volume about 25 c.c.). All determinations were carried out in duplicate (using 16–60 grams of the metals). The difference between two of these

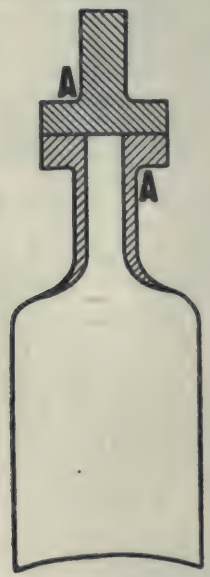


FIG. 1.

never exceeded three units in the third decimal place. Toluene (or water) was used as the liquid in the pycnometer, but as a control we sometimes substituted paraffin oil for it. The thermometers in our thermostat (the temperature of which was kept constant within some thousandths of a degree) had been compared with a standard of the Phys.-Techn. Reichsanstalt at Charlottenburg, Berlin.

8. We received the cadmium (bars) in two consignments, which we shall distinguish by the letters K_1 and K_2. The metal was reduced to turnings on a lathe, washed with dilute hydrochloric acid, water, alcohol, ether, and dried *in vacuo* over sulphuric acid. The density of K_1 we found to be :

$$d\,{}^{25^\circ}_{4^\circ}\ 8{\cdot}635\ ;\ 8{\cdot}632\ ;\ 8{\cdot}633\ ;\ \text{mean } 8{\cdot}633$$

in independent determinations, taking fresh quantities each time.

* *Journ. Americ. Chem. Soc.*, **34**, 563 (1912).

For K_2 we found :

$$d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}641\ ;\ 8{\cdot}644\ ;\ 8{\cdot}642\ ;\ \text{mean } \mathbf{8{\cdot}643}.$$

9. After heating K_1 at a temperature of 150° during 95 hours in a current of dry carbon dioxide which was freed from oxygen, we found :

$$d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}630 \text{ and } 8{\cdot}633.$$

These figures show that the density of the metal had not been changed by the heating.

10. As there was a possibility that we had passed a transition-point, but that cadmium showed similar retardations to those which we had found in the case of bismuth, we heated a certain amount of K_2 $\left(d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}643\right)$ during 3 days and nights at 100° in contact with a dilute solution of cadmium sulphate. After this time the metal was chilled (at 0°) and washed with water, dilute hydrochloric acid (these liquids had been cooled), alcohol, and ether. It was then dried at 30° *in vacuo* over sulphuric acid. Two determinations gave :

$$d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}633 \text{ and } 8{\cdot}633.$$

This experiment showed that by heating at 100° a change had been produced in the metal which lowered its density (measured at 25°) by 10 units in the third decimal place ; our duplicate determinations prove that this difference exceeds considerably our experimental errors.

11. In order to determine if a change of density takes place at temperatures below 100°, we warmed the metal $\left(d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}633 \text{ and } 8{\cdot}633\right)$ again in contact with a solution of cadmium sulphate for 14 hours at a temperature of 60–70°. After this the metal was chilled, washed, and dried in the manner described above. Its density was now :

$$d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}620,$$

which proves that there occurs at 60–70° a diminution in the density of 11 units in the third decimal place.

12. We repeated the experiment described in §11 with the specimen the density of which was now $d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}620$, keeping it this time for 24 hours at 40°. We found : $d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}642$ and $8{\cdot}643$. Its density (taken at 25°) showed an *increase* of 22 units in the third decimal place.

13. The experiment of §11 was repeated again with the metal that had now a density of $d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}642$ (8·643). After having kept it for 24 hours at 60–70° in a solution of cadmium sulphate, we found after chilling, washing, etc. :

$$d\,\frac{25^\circ}{4^\circ}\ 8{\cdot}631 \text{ and } 8{\cdot}633.$$

At 60–70° there has been again a *decrease* of 10 units in the third decimal place.

14. The experiments described above show that cadmium is able to

undergo a *reversible* transformation. It may be pointed out here that all the changes we are treating of here are *reversible* ones.

15. In order to fix the transition temperature of cadmium more closely we carried out a series of

2. *Experiments with the Dilatometer.*

16. In order to measure as accurately as possible the changes of volume which the metal undergoes in short periods of time we used 360 grams of our metal K_2. We heated it for 24 hours in contact with a solution of cadmium sulphate. It was then chilled, washed, dried, and transferred into a dilatometer, which was then filled with paraffin oil. This had been heated for some hours at 200° under reduced pressure in contact with finely divided cadmium, until there was no more evolution of gas bubbles. In order to reduce as far as possible the quantity of this oil, the expansion of which would have made the measurements more troublesome, a quantity of small glass beads was put into the bulb.

The dilatometer was now kept at different but constant temperatures by means of an electrically heated thermostat,* the temperature of which remained constant within 0·002 degree. (A Beckmann thermometer was used.) By this device the dilatometer † becomes an instrument of precision.

17. The results are given in Table I.

TABLE I.

Temperature.	Duration of the Observations in Hours.	Rise of the Level of Oil in mm.	Rise in mm. per Hour.
49·60°	10½	— 1,500	— 170
59·60°	5	— 233	— 46
60·45°	3½	— 66	— 19
62·40°	9½	— 74	— 8
64·90°	4	0	0
66·90°	16½	+ 53	+ 3
84·40°	6	+ 267	+ 44

From these measurements one might conclude that there is a transition-point at 64·9°. However, our investigations on copper and zinc had shown that such a transition-point may be changed by varying the previous thermal history of the metal.

If there were simultaneously present more than two allotropic modifications of the metal this behaviour might be expected.

18. We also found in the case of cadmium that the transition temperature changes in varying the previous thermal history of the metal. The following experiments may be mentioned in this connexion.

19. A certain quantity of cadmium (K_4) was divided in two parts [$(K_4)_1$ and $(K_4)_2$] of 500 grams each. $(K_4)_1$ was reduced into turnings on a lathe and immediately put into a dilatometer. At 69·9° we observed a *decrease* of volume (469 mm. in 25¼ hours).

20. $(K_4)_2$ was converted into turnings in the same way and kept for 5 days and nights at 100° in a solution of cadmium sulphate. After having it put into a dilatometer we made the readings shown in Table II.

* Its description has been given in full in the paper, *Zeitschr. f. physik. Chemie*, **87**, 409 (1914).

† The capillary tube (diameter of bore 1 mm.) was bent into a horizontal position.

TABLE II.

Temperature.	Duration of the Observations in Hours.	Rise of the Level of Oil in mm.	Rise in mm. per Hour.
49·6°	$\frac{1}{6}$	− 100	− 600
60·4°	$\frac{1}{2}$	− 125	− 250
62·5°	$\frac{2}{3}$	− 14	− 21
63·1°	$\frac{1}{3}$	+ 15	+ 45
63·7°	$\frac{1}{3}$	+ 83	+ 249
69·6°	$\frac{1}{12}$	+ 225	+ 2,700

The transition-point is 62·8°.

21. The metal was now kept at 100° in contact with a solution of cadmium sulphate for 7 days and nights. After this it was put into a dilatometer, which was heated for 24 hours at 145°, then for 24 hours at 270° (that is, only 50° below the melting-point of the metal).

We only succeeded in "bringing it into motion" by heating the metal for 48 hours at 50° in a solution of the sulphate. We then got the following results:

TABLE III.

Temperature.	Duration of the Observations in Hours.	Rise of the Level of Oil in mm.	Rise in mm. per Hour.
60·0°	$\frac{1}{2}$	− 105	− 210
63·0°	$\frac{1}{3}$	− 11	− 33
63·5°	$1\frac{1}{6}$	− 8	− 6
64·0°	$1\frac{1}{6}$	+ 22	+ 18
69·0°	$\frac{1}{6}$	+ 58	+ 348

The transition-point has been changed to 63·4°.

22. In this way we carried out a great many experiments on samples with different previous thermal histories. The extreme limits which were found for this (apparent) transition temperature were 69·3° and 61·3°.

23. The experiments described above show that it is very difficult, if not impossible, to fix the real transition-point of the pure modifications in this way. We therefore tried to prepare a sharply defined modification of cadmium avoiding high temperatures.

24. For this purpose we electrolysed an ammoniacal solution of cadmium sulphate between an electrode of platinum and one of pure cadmium (40 volts, 20–25 amperes, surface of the electrodes 26 cm.²).

We kept the temperature of the solution below 40°, cooling the vessel with ice. The solution was kept homogeneous by a glass stirrer (Witt), which was rotated by a small motor. The cadmium formed at the electrode was washed with dilute sulphuric acid, then with water, alcohol, and ether. After this it was dried at 40°.

25. One hundred and seventy grams of this material were put into a dilatometer. As it is very finely divided, great care must be taken in order to remove the air from the apparatus. We used a Gaede pump for the

purpose. The paraffin oil was boiled on this pump with finely divided cadmium.

26. If there had been formed during the electrolysis only one modification of cadmium we might expect that no transformation would occur in the dilatometer, in consequence of the absence of germs of a second form. From our earlier experiments we know that even if a second modification were present the retardation may be very strongly marked.

27. We found in our first experiment with this cadmium which had been electrolytically deposited that neither at 50°, nor at 80°, nor at 100° did any change occur.

28. After having removed the paraffin oil we washed the metal with ether and brought it in contact with a solution of cadmium sulphate (12 hours at 100°, 48 hours at 50°). After this the dilatometer gave the following results:

TABLE IV.

Temperature.	Duration of the Observations in Hours.	Rise of the Level of Oil in mm.	Rise in mm. per Hour.
71·0°	¾	− 351	− 468
94·8°	¼	+ 132	+ 528
70·5°	5¾	− 267	− 46
70·5°	11	+ 47	+ 4
60·0°	24	− 138	− 6
70·0°	1½	+ 70	+ 46
65·0°	1½	− 53	− 38

There is a change in the direction of motion of the meniscus at a constant temperature (70·5°).

29. This change proves that now (viz. after the treatment of the metal at 100° and 50° with a solution of cadmium sulphate) there are simultaneously present more than two modifications.

30. Our next task consisted in identifying the product which is formed during the electrolysis of solutions of cadmium salts. It may be pointed out here that I found in collaboration with Dr. E. Goldschmidt that when a solution of tin salts is electrolysed below 18°C. there is not formed *grey* tin, as might be expected, but the modification which is *metastable* at this temperature.

3. *The Electromotive Behaviour of Cadmium.*

31. Some years ago Professor Hulett at Princeton described* "a low voltage standard cell," represented by the following scheme:

Cd	Solution of cadmium sulphate of arbitrary concentration	Cd amalgam 12·5 per cent. Cd by weight.

The e.m.f. of this combination is 0·0505 volt at 25°. The reproducibility is about 0·5 millivolt. The cadmium electrode of the cell has to be electrolytically deposited in order to give a definite potential.†

* *Trans. Americ. Electrochem. Soc.*, **7**, 353 (1905).
† Th. W. Richards and Lewis, *Zeitschr. f. physik. Chemie*, **28**, 1 (1899).

32. By an exhaustive investigation of these cells we were able to prove that some disturbances, observed by Hulett, could be avoided if their formation were carried out in a special way. The e.m.f. is then immediately after construction 0·0503 volt at 25°, and generally remains constant.

33. All determinations to be described below were carried out by the Poggendorff compensation method. The resistances used had been checked by the Physikalisch-Technische Reichsanstalt at Charlottenburg, Berlin. Our two standard elements (Weston) were put into a thermostat which was kept at 25°. We used as a zero instrument a Deprez-d'Arsonval galvanometer. It was mounted on a vibration-free suspension (Julius). The readings were made by means of a telescope and scale; 0·02 millivolt could easily be measured.

34. Our dilatometric measurements with cadmium which had been electrolytically deposited gave the result that this material only undergoes transformation at temperatures below 100° if it has been in contact at 50° (100°) with a solution of cadmium sulphate (comp. § 28). The probable and obvious conclusion is that by electrolysis we get exclusively γ-cadmium, the modification which is stable at high temperatures. If this were the case the γ-cadmium would be transformed into β-cadmium at 100°, into α-cadmium at 50° in contact with the solution of the sulphate. If now the γ modification is really generated by electrolysis (analogous to what happens with solutions of tin salts), the Hulett cells (H.C.) which have been studied until now would contain this material as the negative electrode.

If this modification happened to be transformed into the modification which is stable at ordinary temperatures and pressure (1 atm.), this would manifest itself by a *decrease* in the e.m.f. of these cells.

35. On the one hand we are working in this case under extraordinary favourable circumstances for stabilization (change into the α modification), as the material, formed electrolytically, is in a very fine state of division and surrounded by an electrolyte, while the quantity which has to undergo transformation is very small. (The electrode is formed by 20 or 30 mgrs. of the metal deposited on a platinum spiral.) Consequently the transformation, if it occurs, will be finished in a short space of time.

36. On the other hand, and this is to be borne in mind in researches of this kind, the possibility exists that the transformation which has to take place *spontaneously* may be suspended, if the metal deposited by electrolysis forms only one single modification, as the germs needed for transformation are then absent.

37. That stability generally does not occur is shown by our dilatometric observations as well as by many other facts, i.e. by the experiments of W. Jaeger,* Ernst Cohen,† Bijl,‡ and Hulett,§ who all found the same e.m.f. (50 millivolts at 25°) for cells which were constructed according to the scheme:

Cd electrolytically deposited	Solution of cadmium sulphate	Cd amalgam 12·5 per cent. by weight.

How obviously the transformation may be delayed might also be inferred from Hulett's words‖: "Many of these cells are still in good order after five years."

* *Wied. Ann.*, **65**, 106 (1898).
† *Zeitschr. f. physik. Chemie*, **34**, 612 (1900).
‡ Ibid., **41**, 641 (1902).
§ *Trans. Americ. Chem. Soc.*, **7**, 333 (1905).
‖ Ibid., **15**, 435 (1909).

This would be in perfect accordance with our own experiences: Clark cells which contain $ZnSO_4 \cdot 6H_2O$ as solid depolarizer preserved their e.m.f. for five years notwithstanding their having been standing at room temperature, i.e. 25 degrees below the transition-point of $ZnSO_4 \cdot 6H_2O$. As in the case of Hulett's cells they had been sealed up after formation.

38. On account of these observations it might be expected that even under circumstances favourable to a transformation (stabilization) of the negative electrode, only a certain number of H.C. would show the transformation.

39. On December 11, 1913, we prepared three H.C. (Nos. 1, 2, and 5) in the following way: We put two platinum spirals into the H-shaped tube B (Fig. 2). Into the right-side tube we put some 1 per cent. (by weight) cadmium

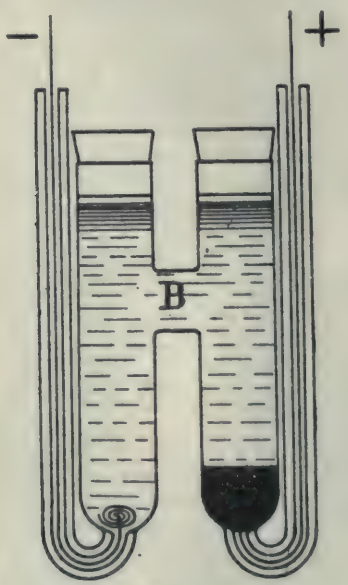


FIG. 2.

amalgam. This amalgam is a fluid at ordinary temperature. We filled the tubes with a dilute solution of cadmium sulphate (half saturated at 15°). After this a current of 1 or 2 milliamperes (1 or 2 mgrs. Cd per hour) was passed from the amalgam to the platinum spiral. After having deposited 20 or 30 mgrs. of cadmium on the left-hand spiral, the capillary tube on the right was brought into connexion with a water-pump in order to remove the amalgam. A number of small pieces of 12·5 per cent. amalgam were then substituted for this.

40. These cells gave at once an e.m.f. of 0·0503 volt when they were put into a thermostat at 25° C. After standing for two months at room temperature the cells were measured again on February 26, 1914. The e.m.f. of 1, 2, and 5 had *decreased* to 0·0475 volt at 25° C., and this value remained unchanged. As might have been expected, the e.m.f. had *decreased* by stabilization of the cadmium.*

41. We prepared two new cells (Nos. 6 and 7) in the same way as 1, 2, and 5. Immediately after the preparation their e.m.f.s were 0·04847 and

* We prepared a large number of these cells: generally 30 per cent. of them showed stability.

0·04795 volt respectively. Some days later their values became constant: 0·04788 and 0·04778 volt. Stabilization had begun already during electrolysis.

42. As our dilatometric measurements had shown that stabilization occurs with great velocity at 50°, we prepared cells (C and O) at 47·9°. The dilute amalgam was then taken out and an 8·5 per cent. (by weight) amalgam was put in, while a fresh solution of cadmium sulphate was used. We substituted an 8·5 per cent. amalgam for a 12·5 per cent. as our intention was to measure these cells also at 0° C. At this temperature the 12·5 per cent. amalgam is a monophase system and such a system must not be used.*

In this way we found at 25° C.:

Cell C: 0·04745 volt.
Cell O: 0·05022 volt.

The cadmium in cell C had thus been stabilized at 47·9°.

43. In order to check the results found up to this point, we also determined the e.m.f. of our stable and metastable cells at 0° C. If the differences in e.m.f. at 25° between the different cells were really to be ascribed to the presence of α-cadmium (cell C) and γ-cadmium (cell O), the difference, which was at 25° C. 2·8 millivolt, ought to *increase* at 0° C., as we are at that temperature at a greater distance from the metastable transition-point

$$\alpha\text{-cadmium} \rightleftarrows \gamma\text{-cadmium}.$$

The measurements at 0° C. gave the following results:

Cell C: 0·05225 volt.
Cell O: 0·05626 volt.

While the difference was 2·8 millivolt at 25° C. it has increased, as might be expected, to 4·0 millivolt at 0° C.

44. Several phenomena which have been described by Hulett, but which are obscure until now, may find an explanation in the light of our experiments. Hulett says: "A number of cells were made with addition of $Cd(OH)_2$, thinking this might make a more uniform cadmium deposit; also the air was completely removed from three before sealing, and in others the air was removed and the cell saturated with nitrogen and with hydrogen. All these gave very variable results, but in each case only 10 mgrs. of cadmium had been deposited on the spiral, and I have lately learned this is too little cadmium, since some cells prepared as above described, excepting that only 10 mgrs. of cadmium was deposited on each spiral, showed the same irregularities and tendency to constantly decreasing electromotive force. These cells were recently all discharged, and then, reversing the current, about 26 mgrs. of cadmium were deposited on each platinum spiral, and they seem to be all coming together nicely and to the value indicated by the old cells."

45. Our observations agree perfectly with those of Hulett, but we have to add the following restrictions: A number of our cells in which only 10 mgrs. of cadmium were deposited, indicated immediately after formation an e.m.f. of 0·0502 volt at 25° C. which *decreased* during two days. Then it became constant: 0·047 volt. Transformation into α-cadmium had consequently occurred; the fact that only a small quantity of cadmium is present causes the e.m.f. to reach very soon its definite lowest value. The phenomenon observed by Hulett is therefore the quick stabilization of γ-cadmium.

46. Professor Hulett has been kind enough to communicate to us the following facts: "Twelve cells which had been sealed after formation

* Bijl, *Zeitschr. f. physik. Chemie*, **41**, 641 (1902).

remained unchanged from March 18, 1905, to May 7, 1914, i.e. during nine years. Their e.m.f. has been during all this time 0·0505 volt. The quantity of cadmium on the spirals varies between 3·7 and 13·7 mgrs. of cadmium."

47. The decrease of e.m.f. which has been observed with cells which contain only 10 mgrs. of cadmium is consequently not to be ascribed to the minute quantity of metal* deposited on the spirals; this quantity is much less in the cells which have been constant during nine years. The reason of the decrease in e.m.f. of those cells is the transformation of γ-cadmium into α-cadmium.

48. In order to check this conclusion we prepared a number of cells (at room temperature) which only contained 5 mgrs. of cadmium on the spirals.

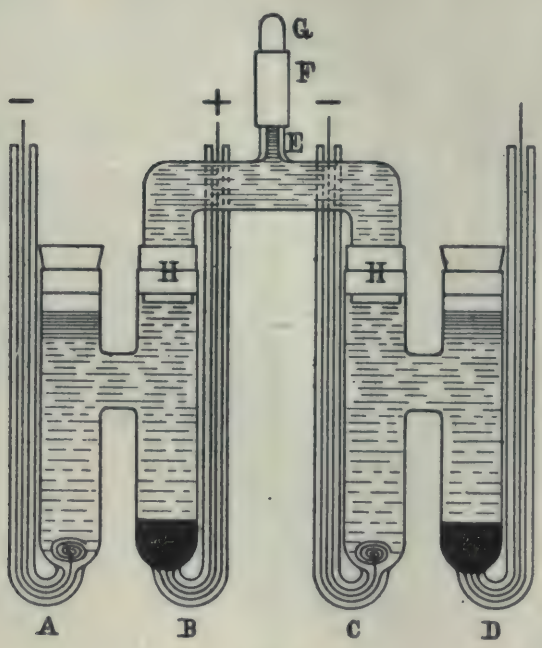


FIG. 3.

Some of these remained metastable (0·050 volt), while others were transformed into the stable form (0·047 volt) after some days.

49. Up to the present we have only directed attention to the electromotive behaviour of α- and γ-cadmium; the β modification has not been mentioned hitherto. However, we were struck by the fact that when constructing a large number of Hulett cells we often got ones which had an e.m.f. of 0·048 volt at 25° C. The e.m.f. of cells which originally had an e.m.f. of 0·050 volt at this temperature spontaneously *decreased* till the value 0·048 volt was reached. After this their e.m.f. remained constant.

* Oberbeck found [*Wied. Ann.*, **31**, 337 (1887)] that a layer of metal A of 2×10^{-6} mm. suffices to give to a metal on which it has been deposited the potential of A. As the surface of the spirals in the H.C. was 0·28 cm.² the layer of cadmium deposited is much thicker.

The conclusion was plain that the cells giving 0·048 volt might contain β-cadmium, those giving 0·047 volt α-cadmium, whilst those giving 0·050 volt have γ-cadmium as a negative electrode.

50. In order to ascertain if the e.m.f of the β cells has a real significance, experiments were carried out on the following lines : At temperatures above the transition-point of the change α-cadmium $\rightleftarrows$ β-cadmium (which we found in the neighbourhood of 60° by dilatometric measurements) the e.m.f. of α cells must be higher than that of β cells. In cooling the cells below the transition-point mentioned the contrary will occur.

51. Our experiments in this direction we carried out in the following way : We constructed a large number of Hulett cells ; one of these, the e.m.f. of which had been originally 0·050 volt at 25° C., had an e.m.f. of 0·047 volt (at 25°) after having been kept for 4 weeks at 47·5°. After this time it remained constant. We combined this cell (No. 7) with another one (No. 22), the e.m.f. of which was 0·048 volt at 25°. The two cells AB (No. 7) and CD (No. 22) (Fig. 3) were connected by a siphon H, which contained the *same* solution of cadmium sulphate as was present in the cells.

The lateral tube E of the siphon was closed by a rubber tube F in which was put a glass rod G. The little apparatus was brought into a thermostat which could be kept at will at 25° or 64·5°.

52. We measured the e.m.f. between the cadmium which had been electrolytically deposited on the platinum spirals A and C against the *common* amalgam electrode B (12·5 per cent. by weight). It is absolutely necessary to use a *common* electrode as the cadmium amalgam of 12·5 per cent. by weight does not form a heterogeneous system at 64·5° ; its e.m.f. is then a function of its composition. The use of the *two* amalgam electrodes B and D might give rise to serious mistakes if there were only small differences in their composition.

The *absolute* e.m.f. of our amalgam electrode against the cadmium in A and C does not play any rôle in our measurements.

53. Table V gives the results of the first series :

TABLE V.

Temperature 25°.

	E.m.f.
Cell 7	0·04741 volt
Cell 22	0·04815 „

Temperature 64·5°.

Cell 7	0·04029 volt
Cell 22	0·03979 „

After having brought the cells to 25° we found :

Cell 7	0·04741 volt
Cell 22	0·04806 „

The table shows that at 64·5° there has taken place an inversion of the poles and that the cells regain their original e.m.f. at 25°.

A second experiment with two cells (Nos. 4 and 8) newly constructed gave the results shown in Table VI.

TABLE VI.

Temperature 25°.

	E.m.f.
Cell 8	0·04757 volt
Cell 4	0·04839 „

Temperature 64·5°.

Cell 8	0·04737 volt
Cell 4	0·04633 „

After having brought the cells to 25° we found :

Cell 8	0·04776 volt
Cell 4	0·04789 „

From Table VI it may be seen that we are here at the limit of measurement obtainable in working with cells of so small an e.m.f., the reproducibility of which is 0·5 millivolt.

54. From the inversion of poles which has been observed we may conclude that the value 0·048 volt at 25° really has significance and is to be attributed to the presence of β-cadmium.

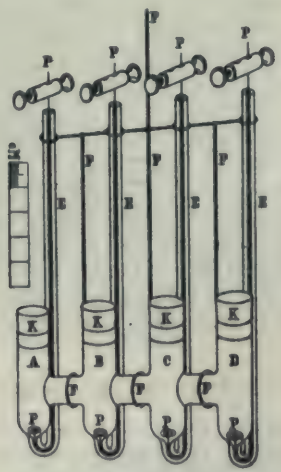


FIG. 4.

55. As our investigations led to the conclusion that a piece of cadmium chosen at random which had been produced from the molten metal contains α-, β- and γ-cadmium, we carried out some measurements in order to check this result.

If such is the case, it might be expected that the potential of such a material against cadmium which has been formed by electrolysis would be zero.

56. We prepared a certain quantity of electrolytic cadmium (Prep. A) and determined at 40° the potential difference between this material in a solution of cadmium sulphate which was half saturated at 15° C. and (1) cadmium (which we received from Kahlbaum in the form of bars) in a finely divided state (Prep. B); (2) cadmium which we had used in our dilatometric measurements; in this material the presence of γ-cadmium was presumed (Prep. C).

Making use of the small apparatus shown in Fig. 4, we first determined the potential difference between two samples of the same material, subsequently that between samples of different preparations. In this way we found:

E.m.f. of A against A = 0·000037 volt
" B " B = 0·000018 "
" C " C = 0·00000 "
" A " B = 0·000037 "
" A " C = 0·000037 "

57. From these measurements we see that γ-cadmium is really present in our preparations, as the dilatometer had shown.

58. We already pointed out above that the example of lead is also particularly instructive. It may be treated here in a few words.

A year ago we carried out some experiments on the behaviour of lead, but the results were negative. However, some time ago we received a letter from Mr. Hans Heller at Leipsic, in which he described some experiments in this direction which may be summarized as follows: He electrolysed a solution of lead acetate (to which some nitric acid had been added) between lead plates in order to generate a *lead tree*. After the experiment, the plates having been standing for three weeks in contact with the solution, they had lost their softness and tensibility; they formed then a brittle and crumbling mass.

Inoculating a plate of ordinary pure lead with the brittle material in contact with the solution mentioned above, Heller observed that the plate fell to pieces.

59. Repeating these experiments, we were able to corroborate the statements made by Heller.

Fig. 5 shows a plate of pure lead in its original condition. Fig. 6 represents the plate having been in contact with a solution of lead acetate* during some days (temperature 15°); Fig. 7 shows it after three weeks in the same conditions. The photographs are natural size.

60. We then carried out an investigation with the pycnometer and the dilatometer in the same way as we did with cadmium and the other metals experimented with.

The density of the metal, which had been originally $d\,\frac{25°}{4°}$ 11·324, *increased* to 11·341, the metal having been in contact with the solution at 15° during 3 weeks. At 50° (5 × 24 hours) the density *decreased* and became $d\,\frac{25°}{4°}$ 11·313. At 25° (6 × 24 hours) it *increased* again and became $d\,\frac{25°}{4°}$ 11·328.

61. Our dilatometric measurements gave the following results:

At 50·8° the *decrease* of the level was 700 mm. (34 hours).
" 74·4° " *rise* " " " 275 " (2¾ hours).

62. From the measurements of §§ 60 and 61 we may conclude that there are more than two allotropic forms simultaneously present.

63. Special attention may be paid to the following phenomenon, which stands in direct relation to the conclusion mentioned: It is generally known that when a bar of any metal which is more electro-negative (resp. electro-positive) than lead is suspended in a solution of a lead salt, the lead is thrown out of solution and a *lead tree* is formed. We stated that the same phenomenon occurred when our pure lead was placed in the solution mentioned

* The composition of the solution was: 400 grams of lead acetate in 1,000 c.c. of water; 100 c.c. of nitric acid (density 1·16 at 15°) were added.

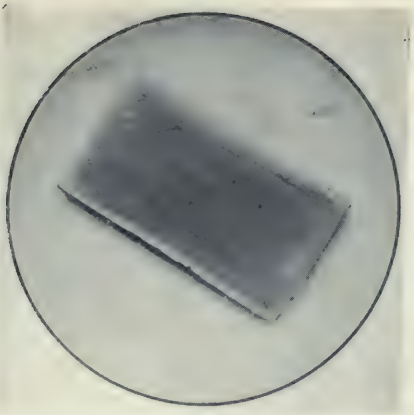


FIG. 5

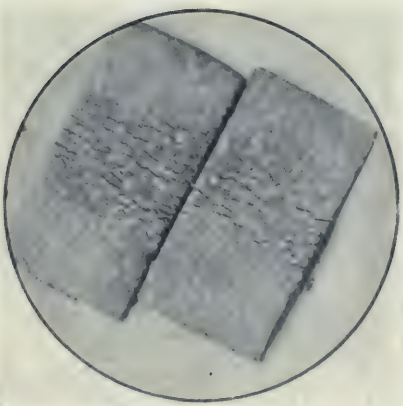


FIG. 6.

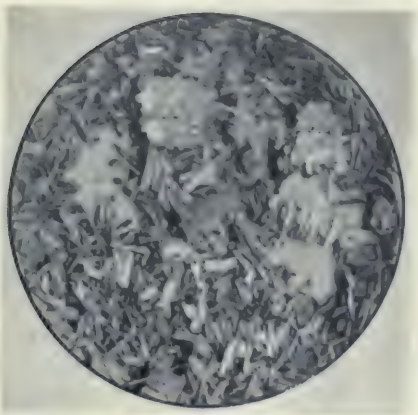


FIG. 7.

above or in a (neutral) solution of lead nitrate. Both at room temperature or at higher temperatures (50°) a lead tree was formed within some days.

64. With lead we are in especially favourable circumstances to observe these phenomena. The electric current which is generated between the stable and metastable modifications which are present simultaneously electrolyses the solution. The metal which is formed electrolytically shows in this case a characteristic form (lead tree), so that the phenomenon is very striking.

65. Finally it may be pointed out here that Theophrast as well as Plutarch seems to have been acquainted with the fact that lead is able to undergo a transformation at low temperatures. Theophrast * (a pupil of Aristotle) says in his book Περὶ Πυρός : *κασσίτερον γάρ φασι καὶ μόλιβδον ἤδη τακῆναι ἐν τῷ Πόντῳ πάγου καὶ χειμῶνος ὄντος νεανικοῦ, χαλκὸν δὲ ῥαγῆναι.* (It is told that tin and lead melted sometimes in the Pontos when it was very cold during a strong winter and that copper was disintegrated.) Plutarch tells us in his *Symposiaca* that *ἀκόναι μολύβδου* (pieces of lead) melted sometimes when it was very cold.

66. Summarizing the phenomena observed in our investigations on cadmium, lead (bismuth, copper, zinc, antimony), we must conclude that the pure metals as we have known them until now are metastable systems consisting of two (or more) allotropic forms. This is a consequence of the very strongly marked retardation which accompanies the reversible change of these allotropic modifications below and above their transition-points. Employing certain devices (adding an electrolyte, using the metals in a very finely divided state), it is possible to increase the transformation velocity in such a degree that the change of the metastable to the stable form occurs within a short time. As such changes are very often accompanied by marked changes of volume, the material is generally disintegrated.

67. As, until now, chemists, physicists, and metallurgists have always dealt with the α, β, γ . . . forms together, all the physical and mechanical constants of metals which have been determined refer to the complicated metastable systems. These are entirely undefined, as the quantities of the α, β, γ modifications they contain are not known.

68. Now it is known that a special physical property of any substance at a definite temperature and pressure depends on its allotropic condition. H. F. Weber found the specific heat of carbon (at 10° C.) to be—

0·1128 in the form of diamond,
0·1604 in the form of graphite,
0·1653 in the form of charcoal.

The following constants were found for white and grey tin :

	White Tin.	Grey Tin.
Density	7·28	5·8
Spec. heat	0·05382	0·04962
Spec. magn. susceptibility ($\times 10^6$)	+ 0·025	− 0·30

With the magnetic susceptibility even the sign is changed.

69. The existing data on the physical constants of metals known until now are thus to be considered as entirely fortuitous values which depend on

* Dr. Ch. M. van Deventer at Utrecht has been kind enough to call our attention to this peculiarity.

the previous thermal history of the material used. Those physical constants which refer to a well-defined condition of the metals are so far unknown. In order to determine these, and only these have a definite signification and are reproducible, we shall have to carry out in the future all measurements for the *pure* α, β, γ . . . modifications of the metals.

70. Reviewing the earlier literature dealing with the specific heat of metals, I found that it contains already a number of data which prove unequivocally that the specific heat of the metals does indeed depend on their previous thermal history.

Le Verrier* stated in a paper published in the year 1892 ("Sur la Chaleur Spécifique des Métaux") that the mean specific heat of copper, silver, zinc, lead, and aluminium remains as a rule constant for periods which do not exceed 200–300°, after which it changes abruptly, as Pionchon† also found in the case of iron, nickel, and cobalt. The variation of the total heat (i.e. the quantity of heat required to raise the temperature of 1 gram of the substance from 0° to t° C.) with the temperature is consequently to be represented by a curve with breaks and not by a continuous one. As a consequence of the retardations in the structural change (*changements d'état*) of the metal, a different value of the total heat is found on cooling from that on heating. If a certain piece of metal is cooled or heated repeatedly, different values for the total heat are found. If we start from a lower temperature and return to it after having overpassed the break in the curve of total heat, a closed and not a single curve is obtained. Thus, while our investigations proved that there exist more than two modifications of copper and lead, the same fact was noted a long time before by Le Verrier, using a different method. The same may be said about aluminium.

71. That others had never observed the phenomena described by Le Verrier may be explained by the fact that they had not heated their preparations *repeatedly* to high temperatures, as he did. We have also observed during our dilatometric measurements that such a transition-point can be overpassed several hundreds of degrees without any effect. If, on the contrary, the metal is repeatedly cooled and heated the transformation is "set going."

72. What has been said about the specific heat holds evidently for every other physical constant. In our paper on the allotropy of bismuth‡ we pointed out that numerous phenomena which had been observed in the study of density, electric conductivity (also under pressure), conductivity for heat, melting-point, thermoelectric force, the Hall effect, etc., and which had not been explained, may find their explanation if the facts recently found are taken into account.

73. In this way a new field of research for chemists, as well as for physicists, presents itself. Whilst it will be the task of the chemist to prepare the pure modifications and study their physicochemical properties, the physicist will require to turn his attention to the determination of their physical and mechanical constants.

74. As the phenomena described here have been unknown up to the present, metallurgists have not been able to take them into account when studying the hardening of metals. And yet these reversible transformations, which often go on so very slowly in consequence of the retardations mentioned above, must play an important rôle when the metals are subjected to changes of temperature.

* *C. R.*, **114**, 907 (1892).

† Ibid., **102**, 675, 1454 (1886); **103**, 1122 (1886). In full: *Ann. de Chim. et de Phys.* (6), **11**, 33 (1887).

‡ *Zeitschr. f. physik. Chemie*, **85**, 419 (1913).

This rôle may become fatal if the metals are in contact with electrolytes (water), as these accelerate enormously the transformation velocity. The volume changes which generally accompany these transformations may cause the disintegration of the materials, as we have shown above. Moreover, it is evident that in those cases where *corrosion* occurs these phenomena have to be taken into account.

VAN'T HOFF LABORATORY, UTRECHT,
November 1914.

APPENDIX, ADDED MARCH 1915.

75. The investigations which have been summarized above have been continued during these last few months. Some of the most interesting results may be mentioned here.

76. Up to the present, heats of transformation of metals have only been determined in one single case. Some months ago Brönsted* carried out some measurements on the heat of the transformation

$$\text{grey tin} \longrightarrow \text{white tin.}$$

He found it to be 532 gram-calories per gram atom of tin at 0° C.

77. For several reasons the calorimetric method used by Brönsted cannot be applied to our case. We therefore carried out our experiments with a *transition cell* of the sixth kind which has been described by Ernst Cohen.† This cell is constructed according to the scheme :—

Electrode of a metal M in its *stable* modification at $t°$ C.	Solution of a salt of M of an arbitrary concentration	Electrode of the metal M in its *metastable* modification at $t°$ C.

78. Hitherto it was impossible to make a quantitative application of this cell, as no metal, having a transition-point, was known which exists in an electrically sharply defined condition.

Our measurements will prove that the transformation α-cadmium $\rightleftarrows$ γ-cadmium is especially suitable for such an investigation.

As we had in view the carrying out of some other measurements with our α- and γ-cadmium, we have not brought them together in one single transition cell, but used them as the negative electrodes in cells which were constructed according to the scheme given by Hulett. These cells were studied separately. Consequently our cells were made up as follows :—

Cd-α	Unsaturated solution of $CdSO_4$ of an arbitrary concentration	Cd-amalgam . . . . . 8 per cent. by weight	(α-cell),

and—

Cd-γ	Unsaturated solution of $CdSO_4$ of an arbitrary concentration	Cd-amalgam . . . . . 8 per cent. by weight	(γ-cell),

* *Zeitschr. f. physik. Chemie*, **88**, 479 (1914).
† Ibid., **30**, 623 (1899).

79. On applying the equation of Gibbs-von Helmholtz—

$$E_e = \frac{E_c}{n\varepsilon} + T\frac{dE_e}{dT}$$

to the α- and γ-cell separately, we find—

$$(E_e)_\alpha = \frac{(E_c)_\alpha}{n\varepsilon} + T\left(\frac{dE_e}{dT}\right)_\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha\text{-cell})$$

and—

$$(E_e)_\gamma = \frac{(E_c)_\gamma}{n\varepsilon} + T\left(\frac{dE_e}{dT}\right)_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma\text{-cell}).$$

$(E_e)_\alpha$ represents the e.m.f. of the α-cell at T°; $(E_c)_\alpha$ the quantity of heat which is generated if at T° one gram atom of α-cadmium is dissolved in an unlimited quantity of cadmium amalgam (8 per cent. by weight). The signification of $(E_e)_\gamma$ and $(E_c)_\gamma$ is quite analogous.

80. From our equations we get—

$$(E_c)_\gamma - (E_c)_\alpha = n\varepsilon\left[(E_e)_\gamma - (E_e)_\alpha - T\left\{\left(\frac{dE_e}{dT}\right)_\gamma - \left(\frac{dE_e}{dT}\right)_\alpha\right\}\right] \quad . \quad . \quad (1)$$

The expression on the left represents the heat of transformation which accompanies the change of 1 gram atom γ-cadmium into α-cadmium at T°, i.e. the value to be determined. Therefore we have only to measure the e.m.f. as well as the temperature coefficient of the α- and γ-cell at T°.

81. As we pointed out above (§ 34), the cells which have been studied by Hulett are our γ-cells. From his determinations between 0° and 40° C. it follows that—

$$(E_e)_\gamma^{t°} = 0{\cdot}05047 - 0{\cdot}0002437\,(t-25) \text{ volt} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

82. We constructed our α-cells starting from γ-cells in which the γ-cadmium was transformed into α-cadmium. The way in which these γ-cells were prepared and in which their e.m.f. was determined has been described above. We prepared 11 γ-cells. At 25° C. their e.m.f. was 0·0504 volt. After standing for a fortnight at 25° the γ-cadmium was transformed into the β modification, as was shown by the fact that the e.m.f. had decreased to 0·048 volt at 25° C. In order to transform the β modification into α-cadmium we put the cells for a fortnight into a thermostat, which was kept at 47·5° C. We now put a fresh amalgam into the cells, while a fresh solution of cadmium sulphate was also introduced. We found that in 4 cells (out of 11) the β-cadmium had been transformed into the α modification. The e.m.f. of these cells was 0·0474 volt at 25° C.

83. They were systematically investigated at 25°, 20°, and 15° C. respectively, in order to determine their temperature coefficients. Table VII contains the results.

The measurements may be represented by the equation—

$$(E_e)_\alpha^{t°} = 0{\cdot}04742 - 0{\cdot}000200\,(t-25) \text{ volt} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

84. The reproducibility of these cells is not less good than that of the γ-cells. Calculating from (3) the e.m.f. of an α-cell at 0° C., the value $(E_e)_\alpha^{0°} = 0{\cdot}05245$ volt is found, while a cell which had formerly been measured at 0° C. (comp. § 43) gave the value 0·05225 volt. This cell had been prepared at a different time, using different materials.

TABLE VII.

E.M.F. of α-Cells (Volt).

Date.	Temperature.	Cell H_2.	Cell H_4.	Cell H_5.	Cell H_6.	Mean.
Jan. 14	25°0	0·04751	0·04740	0·04763	0·04758	
15 a.m.	25·0	0·04725	0·04797	0·04710	0·04714	0·04742
15 p.m.	25·0	0·04721	0·04790	0·04710	0·04710	
16	25·0	0·04728	0·04794	0·04731	0·04731	
Jan. 18	20·0	0·04848	0·04837	—	—	
19 a.m.	20·0	0·04843	0·04833	—	—	
19 p.m.	20·0	0·04849	0·04841	—	—	
19 night	20·0	0·04832	0·04836	—	—	0·04841
20	20·0	0·04840	—	—	—	
21	20·0	0·04843	—	0·04850	0·04860	
22	20·0	0·04833	—	0·04833	0·04843	
Jan. 23 a.m.	15·0	0·04908	—	0·04944	0·04947	
23 p.m.	15·0	0·04925	—	0·04966	0·04968	
24	15·0	0·04959	—	0·04948	0·04956	0·04943
25	15·0	0·04924	—	0·04928	0·04937	
Jan. 25	25·0	0·04752	—	0·04759	0·04761	

85. In order to calculate the heat of transformation of α-cadmium into γ-cadmium at 18° C. we have to introduce the numerical values into our equation (1). From (2) we find—

$$(E_e)_\gamma^{18^\circ} = 0{\cdot}05217 \text{ volt.}$$

$$\left(\frac{dE_e}{dT}\right)_\gamma^{18^\circ} = -0{\cdot}0002437 \frac{\text{volt}}{\text{degree}}.$$

From (3) we get—

$$(E_e)_\alpha^{18^\circ} = 0{\cdot}04885 \text{ volt.}$$

$$\left(\frac{dE_e}{dT}\right)_\alpha^{18^\circ} = -0{\cdot}000200 \frac{\text{volt}}{\text{degree}}.$$

$$(E_e)_\gamma^{18^\circ} - (E_e)_\alpha^{18^\circ} = [0{\cdot}05217 - 0{\cdot}04885 - 291\,(-0{\cdot}0002437 + 0{\cdot}000200)]\,46105$$
$$= 739 \text{ gram calories.}$$

If one gram atom of α-cadmium is transformed into γ-cadmium, the change is accompanied at 18° C. by an absorption of 739 gram calories.

86. It may be pointed out that the temperature at which $(E_e)_\alpha = (E_e)_\gamma$ represents the *metastable* transition-point of the reaction α-cadmium $\rightleftharpoons$ γ-cadmium.

If we put (2) = (3), we find—

$$0{\cdot}00305 = 0{\cdot}0000437\,(t - 25)$$
$$t = 94{\cdot}8^\circ \text{ C.}$$

87. It is evident that the heats of reaction of metals with other substances, as they have been determined hitherto, are indefinite. This has been proved in a special paper.* We also pointed out there that the same is the case with the heats of fusion of metals, and that the values found up to the present show, as was to be expected, very large discrepancies, reaching in some cases 80 per cent. Consequently all thermochemical data of the metals must be redetermined with the pure $\alpha, \beta, \gamma \ldots$ modifications of these substances.

88. In §§ 66–73 it was pointed out that the existing data on the physical and mechanical constants of metals known up to the present are to be considered as entirely fortuitous values, since they refer to the indefinite metastable systems which are produced when metals pass from the molten to the solid state.

89. As for the specific heats of metals, we have already mentioned the determinations of Le Verrier, to which only small attention has been given. In those cases where this has been done, they have generally been considered as less accurate.

90. The fact that different authors have found (at the same temperature) for a certain metal very different values for the specific heat must partly be attributed to their omitting to take into account the previous heat treatment of the metal experimented with. From the enormous material found in the literature, we only quote here the values for bismuth found at 18° C. by L. Lorenz † to be 0·0303, whilst Jaeger and Diesselhorst ‡ give 0·0292. The difference is 3 per cent. But also differences as high as 13 per cent. occur, as might be seen from a paper of Schübel.§

91. That these facts recently have attracted notice on the part of physicists is evident from a paper published by E. H. Griffiths and Ezer Griffiths,‖ who say: "A further possible source of uncertainty is the effect of sudden chilling of a metal when rapidly cooled from a high temperature." However, they do not mention the reasons which led them to this conclusion. As these investigations, as well as those of Ezer Griffiths ¶ on "The Variation with Temperature of the Specific Heat of Sodium in the Solid and Liquid State," play an important rôle in our subsequent arguments, we must dwell upon them.

92. Using a special calorimeter in which the metal was electrically heated, they determined the *true* specific heat of different metals at different temperatures. As the substances were raised from a given temperature through very small ranges of temperature (about 1·4° C.) their previous thermal history was not changed by the experiment itself. Evidently this is of high importance, as in the methods in use up to the present (method of mixtures, ice-calorimeter) the substances are heated to considerably higher temperatures, by which procedure changes may occur which are uncontrollable.

93. The metals used by the authors (of high purity) were *cast*. Evidently they were of opinion that the condition of their material was definite. This is most surprising, as they themselves called attention to the fact that previous thermal treatment must be taken into account. It will be proved once more below that the metals experimented with by Messrs. Griffiths did not correspond to definite states. The values they found for the specific heats of Cu, Ag, Zn, Pb, Al, and Cd must therefore be considered as

* *Proc. Roy. Acad. Amsterdam*, **17**, 926 (1915).
† *Wied. Ann.*, **13**, 437 (1881).
‡ *Abhandl. Phys. Techn. Reichsanstalt*, **3**, 269 (1900).
§ *Zeitschr. f. anorg. Chemie*, **87**, 81 (1914).
‖ *Phil. Trans. Roy. Soc. London*, **213** (A), 119 (1914).
¶ *Proc. Roy. Soc. London*, **89** (A), 561 (1914).

fortuitous values. This is the more to be regretted as their measurements were carried out with the greatest care.

94. We shall now consider the experiments on sodium. The high importance of this research with respect to the question which occupies us may be characterized by the following four points—

(*a*) The previous thermal history of the pure metal was strictly defined.

(*b*) Every value given for the *true* specific heat is the mean of 4 or 6 independent determinations which are carried out under varying conditions (change of the quantity of electric energy supplied). As Tables VIII and IX show, the agreement of the measurements is perfect.

(*c*) The determinations have been carried out with the *solid* metal from 0° C. up to the melting-point.

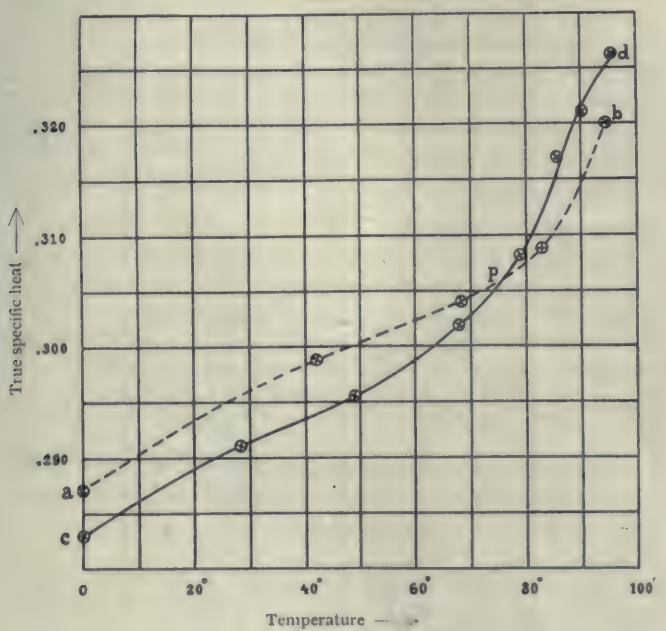


FIG. 8.

(*d*) The author has exclusively taken the standpoint of experimental physicists, giving his quantitative results without any commentary.

95. Concerning the item (*a*) the following may be pointed out. The author had found that the true specific heat of *molten* sodium can be reproduced with great accuracy, even if the previous heat treatment of the *molten* metal is changed within wide limits. The contrary occurs with the *solid* metal; discrepancies of 2 per cent. at the same temperature were found in his early experiments. Referring to this result he says: "The importance of this point was not sufficiently realized in the early determinations, and a large number of otherwise excellent experiments have been rendered worthless through lack of attention to the precise nature of the previous heat treatment."

96. The metal used in the final experiments was prepared as follows:

TABLE VIII.

Na—slowly cooled (Annealed).

Temperature.	Data.	Spec. Heat.	Mean.
0°	Aug. 28	0·2835 0·2836 0·2820 0·2826	0·2829
28·82°	Aug. 19	0·2911 0·2910 0·2929 0·2893	0·2910
49·38°	Aug. 8	0·2954 0·2952 0·2951 0·2955 0·2951 0·2955	0·2953
49·27°	Aug. 16	0·2946 0·2949 0·2964	0·2953
49·07°	Aug. 17 Aug. 20	0·2963 0·2945 0·2942	0·2950
67·79°	Aug. 21	0·3014 0·3037 0·3018 0·3010 0·3018	0·3019
79·15°	Aug. 22	0·3083 0·3085 0·3086 0·3079	0·3083
85·65°	Aug. 15	0·3168 0·3181 0·3165 0·3178 0·3159	0·3171
90·03°	Aug. 23	0·3209 0·3208 0·3208 0·3210	0·3209
95·53°	Aug. 24	0·3260 0·3254 0·3260	0·3258

"*Annealed*" (Table VIII). The rate of cooling from the liquid state was less than 4° per hour, which was the rate of fall of the bath from 100° to 86° C. "*Quenched*" (Table IX). The metal was heated in an oil bath to 130° C., and then rapidly transferred to a vessel of ice-cold water. The metal was enclosed in a case of copper of special form. The determinations with the quenched metal were made starting from the lowest temperature (0° C.) and progressing in steps up to 95° C. If the cooling had taken place very slowly, the values found at each temperature were definite and reproducible. This proves that the values given in Table VIII refer to the *state of equilibrium* as the corresponding temperature.

The measurements of August 8th, giving the value 0·2953 (at 49·38°) having been completed, the metal was taken out of the calorimeter, heated up to 100° (melted) and allowed to cool *rapidly* in air. The value then obtained for the specific heat (at 49·38°) was 0·3014. Again heating to 100° (melting) and allowing to cool *very slowly* gave the value 0·2953 (at 49·38°), identical with the value previously obtained for the "annealed" metal.

97. The diagram (Fig. 8) represents the results graphically. The broken line Apb represents the results of the determinations after the sodium had been quenched, whilst the curve Cpd represents those concerning the annealed metal. Considering the figure more closely, it is evident that sodium is enantiotropic or monotropic; this was not known up to the present.*

98. We have here for the first time a case where it is possible to obtain at will, and in nearly quantitative yield, either the stable or the metastable solid modification from a metallic melt. Until now I have not been able to get this result in my investigations on bismuth, copper, zinc, antimony, and lead. In these cases the different modifications were always simultaneously present in the material experimented with. Only with cadmium I have succeeded in preparing the pure α, β and γ modifications by preparing electrolytically the γ-form, which was transformed afterwards into the β or α modification.

99. From the work carried out by myself and my collaborators it follows that a piece of sodium, chosen at random, is at ordinary temperatures in a metastable condition, as there are simultaneously present both the α- and β-sodium.

100. This conclusion is proved in a quantitative way by the very exact measurements of Ezer Griffiths. It is to be expected that sodium which has received heat treatment of an intermediate character (between chilling and annealing) will have at a given temperature a specific heat between the values found at the same temperature for the chilled and annealed material respectively.

101. The following experiment proves that this is really the case: The metal was melted and allowed to cool freely in air (Samples A and B, Table X). Whilst the specific heat of the annealed metal was found to be 0·2829 at 0° C. and that of the chilled 0·2870, the experiment gave now (at 0° C.) the values of Table X.

The specific heat values are found now between 0·2829 and 0·2870.

Griffiths says: "Several determinations were made at temperatures between 88° and 94° after a somewhat similar heat treatment, and the same feature is common to all, the values falling between the extremes corresponding to the annealed and the quenched states."

* Schädler [*Lieb. Ann.*, **20**, 2 (1836)] thinks it probable that sodium crystallizes in the regular system, whilst Long [*Journ. Chem. Soc.*, **13**, 122 (1860)] found that it is also able to crystallize in the quadratic system.

TABLE IX.

Na—"quenched."

Temperature.	Data.	Spec. Heat.	Mean.
0°	Aug. 29	0·2892 0·2874 0·2864 0·2852	0·2870
40·16°	Aug. 30	0·2973 0·3002 0·2953 0·2992 0·2983	0·2981
68·60°	Aug. 31	0·3024 0·3049 0·3073	0·3040
68·60°	Sept. 2	0·3034 0·3020 0·3038	
82·15°	Sept. 3	0·3087 0·3094 0·3095 0·3079	0·3089
94·02°	Sept. 4	0·3195 0·3213 0·3192 0·3200	0·3200

TABLE X.

Preparation.	Date.	Spec. Heat at 0° C.	Mean.
A	April 7	0·2861 0·2868 0·2866 0·2864 0·2858	0·2864
B	June 4	0·2864 0·2871	0·2863
	June 5	0·2862 0·2855	
	June 6	0·2864 0·2863	

102. These experiments consequently prove in a quantitative way that sodium, as it has been known up to the present, is also a metastable system in consequence of allotropy and that the physical (and mechanical) constants of this metal which have been determined hitherto are entirely fortuitous values. They must be redetermined with the pure α and β modifications of the metal. The same may be said about potassium.

VAN'T HOFF LABORATORY, UTRECHT,
March 1915.

THE PART PLAYED BY THE AMORPHOUS PHASE IN THE HARDENING OF STEELS.

Mr. J. C. W. Humfrey, B.A., M.Sc., M.Eng. (Sheffield), read a Paper on "The Part Played by the Amorphous Phase in the Hardening of Steels."

The existence in solid metals of an amorphous or undercooled liquid phase has already been deduced from two distinct points of view, viz. :—

1. As being formed in the crystal gliding planes when a metal is severely overstrained. This phenomenon has been particularly studied by Beilby.

2. As normally existing as a thin film or cement between the individual crystals of which a mass of metal is built up. This theory, which was originally independently advanced by several writers, has received strong experimental support from the work of Rosenhain and Ewen, and the present author.[1–4]

In a paper[4] dealing with the influence of the amorphous intercrystalline cement upon the mechanical properties of metals, the author put forward a suggestion that the recrystallization which occurs in iron and steel at the Ar_1 change-point does not take place directly, but by the preliminary breakdown of the γ crystals to an amorphous state, followed by a subsequent formation of the β or α crystals from the amorphous. The suggestion was advanced in order to explain the continuous existence of an intercrystalline cement in iron irrespective of its allotropic changes. A somewhat similar idea was advanced many years ago by Barus and is quoted by Roberts-Austen in his *Introduction to Metallurgy*, as follows: "When iron passes through the temperature of re-calescence, its molecular condition is for an instant almost chaotic."

In the present paper the suggestion is examined further, and from it is deduced an explanation of the hardening of steels.

In the idea as originally advanced it was assumed that the amorphous cement which exists during the different allotropic ranges of iron is always of a similar nature, and corresponds in phase with that of the true liquid metal; further consideration of the matter has, however, led the author to a somewhat different view, and one, he thinks, in which the theory of the formation of an intermediate amorphous phase during recrystallization becomes more consistent with thermodynamical principles.

We know that a substance, in passing from the liquid to the solid (crystalline) form, changes from a state in which the units are irregularly dispersed to one in which they are arranged in some definite and regular manner, which is characteristic of the substance in question Numerous crystallographic researches—chiefly upon crystals having a perfect external form—have resulted in a theory of crystal structure which the author believes to be now generally accepted, and which has indeed received striking

confirmation from the recent experiments upon the reflection of X-rays from crystal surfaces. The theory in question asserts that the regularity of structure within a crystal is twofold, viz. :—

1. That the centres of gravity of the molecules are arranged together according to one of a series of geometrical devices called "space lattices," in which each point in the lattice is surrounded by a similar distribution of other points.

2. That in each molecule of a crystal the atoms are similarly situated.

The author considers that it is the second form of regularity which essentially gives rise to the first ; or in other words, that in crystallization from fusion it is the forces exerted by each molecule upon its neighbours (i.e. forces due to the resultant reactions of its atoms) which bring about the space-lattice structure of the crystal.

Now an allotropic change must be considered as being essentially accompanied by a change in the internal structure of the molecules, e.g. a reorganization of the atoms composing them or a change in their number. Thus we have the two gaseous allotropes of oxygen, the common gas in which each molecule contains two atoms, and ozone in which each molecule contains three atoms. When an allotropic change takes place in a crystalline body we must imagine a similar internal rearrangement of the atoms in each molecule ; and, if the new form which the molecules take involves a corresponding change in the external forces which they exert upon one another, then the previously existing space lattice may become unstable and a fresh one may be formed characteristic of some other crystal form. But before the reorganization can be completed there must, at least temporarily, be a state of disorder, and it is during this disorder that the author considers that the structure must be considered as amorphous. The intermediate amorphous state may be realized as corresponding to the liquid which would be formed by the fusion of the solid phase stable at the lower temperatures, if the conditions could be so adjusted that the subsequent recrystallization were avoided. Certain cases are known where such a phenomenon can be actually observed. Thus in the case of sulphur the change from the monoclinic to the rhombic and *vice versa* normally occurs at a temperature of 95·6° C. ; but the rhombic form stable below this temperature can be heated above it, and in this metastable condition melts at 115° C. ; if, however, the change to monoclinic is allowed to complete itself before this temperature is reached, the monoclinic crystals of sulphur do not melt until 120° C.

In the case of iron the temperature-tenacity curves obtained by Rosenhain and the present author [3] give strong indications that a similar phenomenon might occur, the rapid drop in the tenacity of both α and β iron before Ac_3 strongly suggesting that they are rapidly approaching their melting-points ; and that if on heating a sample of iron suitable conditions of pressure could be applied which prevented the recrystallization to the γ, then a true melting-point could be observed in the neighbourhood of 900° C.

We know that physical changes of state, such as from liquid to solid or from one allotropic modification to another, do not take place instantaneously throughout the whole mass of a body, but that starting from certain nuclei they proceed gradually outwards. Thus we must conceive that the intermediate amorphous phase existing during an allotropic change which occurs normally (i.e. by relatively slow heating or cooling) commences to recrystallize almost as soon as it is formed, and is present at any particular instant during the change merely as thin films or layers between the coexisting crystalline phases, the films moving forward as the change progresses. The course of the breakdown of the one crystalline phase to the amorphous would tend to

follow those planes in which the freedom of movement was greatest, viz. the crystal gliding planes and possibly the intercrystalline boundaries.

That a second crystalline phase may form after the first has broken down to amorphous necessitates the condition that the mass is not too viscous for the forces of crystallization to overcome the viscosity and to marshal the molecules into their new orientation. We know from Beilby's work that such a condition is not invariably present, since he has shown that any amorphous phase formed by severe overstrain in the cold possesses a definite stability up to certain well-marked temperatures, and only passes back into the crystalline state when these temperatures are exceeded. Thus, if an allotropic change be made, by suitable conditions, to take place at a temperature at which an amorphous phase is stable, then we can conceive that while the breakdown from the one crystalline state may take place, yet the fresh crystallization may be prevented, and that under such conditions the amorphous phase formed by the breakdown will persist. That the breakdown from a crystalline to an amorphous state may take place in spite of low temperature is clearly shown by the formation of amorphous from the crystalline by overstrain, and also by the changes in certain alloy steels to be referred to later.

In a metal in which an allotropic change normally takes place at a temperature well above that at which the viscosity is sufficient to prevent crystallization, abnormal conditions—such as rapid cooling—may delay the change to well below this temperature.

From the general considerations which have been advanced above we may now pass to the particular case in view, viz. that of steels. Firstly we have the following experimentally determined data :—

1. Pure iron undergoes an allotropic change at about 860° C., which results in a complete recrystallization. The latter fact has been clearly proved by "heat-reliefs,"[5] by the microscopical study of strain effects,[3] and by other experiments.

2. With increasing percentages of carbon the temperature of the change is gradually lowered until with ·9 per cent. of carbon it occurs at a minimum temperature of 680° C. With less quantities of carbon than ·9 per cent. the change does not take place at one temperature, but a diminishing amount of γ iron (containing the carbon in solid solution) is retained down to 680° C., where the change is finally completed.

3. A second change occurs in iron and in steels containing less than ·45 per cent. of carbon at about 780° C., which change is marked by an evolution of heat on cooling, a discontinuity in the magnetic properties, and a smaller though clearly marked discontinuity in the tenacity. As to how far this change represents a truly allotropic one is a matter of some doubt, but we do know at least that it is *not* accompanied by any recrystallization, and for this reason does not enter into the present argument.

4. Iron at temperatures above the allotropic change-point referred to in (1) is capable of holding carbon in solid solution, but in the state which normally exists below the change-point it is incapable (or practically so) of holding it. While it seems probable that it is held in solution in the form of carbide, it is not definitely known whether it is as the carbide Fe_3C which normally forms when it is thrown out of solution at 680° C. ; certain experiments[6] rather tend to the contrary view.

5. The temperature at which amorphous matter, formed by severe overstrain in the cold, commences to recrystallize freely on subsequent heating, and which conversely may be considered as the minimum temperature at which crystallization can occur in an undercooled liquid mass on cooling,

has been determined for mild steel by Goerens[7] and found to be in the neighbourhood of 500° C. While a certain amount of crystallization can proceed below this temperature, it is very small when compared with that which proceeds when it is attained. It is doubtful, however, whether any very exact limits can be laid down for the maximum temperature below which the amorphous phase is stable. In the cases where it has been formed by overstrain, it is possible that the actual disturbance from the true crystalline orientation may not be the same in all places where an amorphous structure has been formed, and that therefore a lower temperature is needed to bring about sufficient freedom for the return to the crystalline structure where the disturbance has been slight, than it is where the disturbance has been more severe. The fact that to each temperature to which an overstrained specimen is heated, there corresponds a certain amount of recrystallization (which ceases to increase after a certain length of time at that temperature), rather lends support to such a view.

Again, it has been found impossible entirely to destroy by strain all or even the greater part of the crystalline phase, and therefore we do not know whether crystallization in a purely amorphous mass will begin at the same temperature or with the same freedom as it would in a mass in which a considerable proportion of crystalline entities are still present; it would appear that a purely amorphous mass would be the more stable of the two.

When formed by overstrain in a normally cooled steel, the amorphous matter will be derived chiefly from the α ferrite, since the cementite is practically incapable of plastic deformation. When formed, however, by the breakdown of austenite in a carbon steel the amorphous matter will consist of a mixture of iron and iron carbide, and this mixture may not possess the same viscosity as pure iron. This consideration is referred to below from a somewhat different point of view.

Although it is evident from the above that we cannot state a very exact figure for the maximum temperature of stability of an amorphous iron-iron carbide solution, yet it is probable that on heating, the stability must become small in the neighbourhood of 500° C., and that conversely an amorphous solution undercooled below this temperature will possess a certain stability which will rapidly increase on further cooling.

From the experimental data outlined above we see, firstly, that while in the case of pure iron there is a range of about 400° C. between the temperatures at which the breakdown of the γ iron occurs and that at which the recrystallization of α iron becomes difficult, yet in the case of a ·9 per cent. carbon steel the range is reduced to less than 200° C. The probability of retaining by sudden cooling some of the amorphous phase formed by the breakdown of the γ structure is therefore much greater with increasing carbon contents. But there is another factor quite apart from this lowering of the temperature of the change-point which causes the presence of carbon to still further promote the retention. Above the change-point the carbide is in solid solution in the austenite, and when this phase breaks down to amorphous the carbide molecules will still remain closely intermingled with those of the α iron. Now, before the amorphous can recrystallize, the two different kinds of molecules have to segregate, since the carbide is insoluble in either α or β iron. Such segregation must necessarily be a slow process in an undercooled viscous mass, and rapid cooling may easily allow the minimum temperature of crystallization to be passed before it has had time to take place. A somewhat similar argument to this last has already been advanced by Rosenhain,[8] but as a reason rather for the retention of austenite than as hindering the crystallization of α iron from amorphous.[9]

It has been shown by Benedicks[9] that to retain γ iron (austenite) in carbon steels pressure, as well as rapid cooling, is necessary; this fact also follows from the known lowering of the change-points by pressure. Now the change from a crystalline to an amorphous state in metals is, in practically all cases, accompanied by an increase in volume, and in the case under consideration this increase will be still more marked by the fact that crystalline γ iron is denser than crystalline α, and therefore much more so than amorphous α. Thus when a certain amount of γ iron has broken down to amorphous it will occupy more space in the mass and will tend to compress the γ iron that has not already changed and therefore to prevent its doing so. Quenching therefore, besides preventing the crystallization of the amorphous mixture formed by the breakdown of the austenite, may at the same time preserve a certain amount of that austenite unchanged. The more severe the quenching, the more austenite retained, since the rapid increase in rigidity of the amorphous mass as it cools will enable it to exert its pressure more effectively.

The theory of the hardening of steels outlined above depends upon two points: (1) that the temperature of the change-point is lowered by quenching, and (2) that during a normal allotropic change there must exist a temporary amorphous state. The influence of the first point has already been advanced by Grenet,[10] the second now shows how this lowering of the change-point may bring about hardness, since it involves the retention of the amorphous state, and such a state is known to be one of particular hardness in practically all metals.

We may now pass to the consideration of how the theory agrees with, and is consistent with, the known physical properties and microstructure of carbon steels hardened by quenching, and of certain alloy steels which possess a similar hard structure even when slowly cooled.

Physical Properties.—The physical properties of a steel hardened by quenching and of the same material hardened by overstrain are in many ways similar, and strongly point to the idea that a similar form of structure is present. Thus in both cases it has been found that the hard metal possesses a distinctly lower specific gravity than the same samples when annealed. Among other properties in which overstrained and quenched steels vary in a similar manner from the annealed metal may be cited the possession of high retentivity, coercive force, and coefficient of hysteresis. The fact pointed out above, that in overstrained steel the carbide and the iron molecules will remain segregated, while in a quenched steel they will be very intimately mixed in solution, may prevent the similarity from being too close.

Microstructure.—The typical micro-constituent of a quenched steel is martensite, which may—according to the carbon contents and the rate of quenching—vary from an almost structureless mass to a strongly marked duplex structure of interlacing needles, the latter type being characteristic of high carbon contents and rapid cooling. According to the present theory the duplex structure consists of the two phases γ iron (austenite) and an amorphous solution of α iron and carbide; the form in which the two phases occur together being due, as advanced above, to the tendency of the austenite crystals to break up most readily along their gliding planes. Conditions which produce an almost structureless martensite are those under which, while practically all austenite has been able to change to amorphous, yet little or no recrystallization of the amorphous has been possible. Such conditions occur in practice when samples are quenched from not too high a temperature; in such a state a steel should possess its maximum hardness combined with a freedom from internal stresses, and therefore be in the most

favourable condition from a practical point of view. Rapid quenching from too high temperatures, which results in the retention of much of the austenite, will produce a less satisfactory result, since besides the fact that austenite is known to be less hard than the amorphous solution, its presence implies internal stresses and liability to hardening cracks and spontaneous fractures. These points are of course well known to all who have dealt with the hardening of steels.

Alloy Steels.—The present theory of hardening applies with special aptness to the case of certain alloy steels, which acquire a hard structure even when slowly cooled. Alloy steels, of which the nickel-carbon series may be taken as a typical examples, are found when normally cooled to possess three different types of structure according to the percentage of these elements which they contain, viz. (*a*) pearlitic, (*b*) martensitic, or (*c*) austenitic. The increasing percentages of the added elements produce a progressive lowering of the change-point, and it has been found that the structure of type (*a*) occurs in all steels in which the change-point lies above about 400° C.; of type (*b*) in all the steels in which the change-point lies between about 400° C. and atmospheric temperature; and of type (*c*) in all the steels in which the change-point lies below atmospheric temperature. The last type, however, become martensitic if undercooled to below their change-point. These results show that in all the steels in which a change-point occurs below 400° C. —a temperature which corresponds very approximately to that below which we have seen the amorphous phase is stable—possess a structure and a hardness which is similar to that of a quenched carbon steel. The present theory exactly accounts for such a phenomenon, since it states that when the breakdown from the γ condition takes place at a temperature at which the amorphous phase is stable, a hard amorphous structure will persist. The fact that the partial change to amorphous can, and does, occur in these steels in spite of low temperature is evidence that the breakdown of a crystalline condition is possible in spite of low temperature.

Two further points may be emphasized in regard to the bearing of the present theory upon the normal austenitic or martensitic structure of alloy steels.

(1) Cold work applied to an austenitic alloy causes a new and intensely hard phase to appear along the slip planes of the γ crystals,[11, 12] and this phase has been shown to possess all the characteristics of martensite. The quantity produced by a given amount of deformation is out of all proportion to the amount of amorphous phase formed by an equal amount of deformation in other metals. If we consider, as the present theory suggests, that the crystals in an austenitic steel are in most cases within less than 100° C. of a temperature at which they spontaneously change to an amorphous state, it is conceivable that when once a certain breakdown occurs along a slip plane due to the deformation, it may proceed with much greater freedom than it would in the case of an ordinary metal in which no such spontaneous change is involved.

(2) The present theory offers an explanation of the irreversible nature of the changes which occur in alloy steel, i.e. that the change from the austenitic to the martensitic structure takes place at a much lower temperature than the reverse change on heating. It suggests that while the change from the γ state to the amorphous on cooling is independent of low temperature, yet the completion of the change, which would be the recrystallization of the amorphous to α, is prevented by it, and that in consequence the amorphous phase persists. The reverse change of amorphous to γ crystals on heating will be prevented by precisely the same cause, viz. that crystallization of any

kind cannot take place until the viscosity has sufficiently diminished to allow of the necessary molecular movements. It has been found that about 400° C. is the minimum temperature at which the change on heating occurs in any of the series of irreversible alloys, and this temperature may therefore be assumed to be the maximum at which an amorphous solution of iron, nickel, and carbide is stable. It will be remembered that it is the same as the temperature at which the change occurs in the alloys which first show a martensitic structure on normal cooling.

Reference may be made at this point to the "high speed" steels. The recrystallization either on heating or cooling of an amorphous solution will depend particularly upon its viscosity, and the viscosity itself upon the temperature and the composition of the mixture. In high-speed steels we have the two properties, firstly that of air hardening, and secondly that of the stability of the hard structure to high temperatures. The latter property appears to be given to the steels by elements such as chromium, tungsten, etc., which are known to form definite carbides. It appears probable that these carbides act by greatly increasing the viscosity of an amorphous solution containing them, and so allow the amorphous state to remain stable at much higher temperatures.

Tempering.—The tempering of hardened steels will, according to the present theory, consist in the progressive crystallization of the amorphous solution formed by the quenching, but the process is possibly rather more complicated than would at first sight appear to be the case, since, from the experiments of Campbell and Haskins (referred to on page 242) it appears to be accompanied by polymorphic changes in the composition of the carbide. The first segregation of an undercooled solution of α iron and iron carbide would, however, agree very well with Benedick's theory of troostite as a colloidal system. It seems possible that the segregation of the two different kinds of molecules might advance some way before an actual crystalline structure, however fine, is formed; in such a condition the structure would correspond to that of a true liquid colloidal solution. We can in this way distinguish between the two phases troostite and sorbite, the former being a partially segregated amorphous mixture of α iron and iron carbide, while the latter is an extremely fine crystalline mixture of the same constituents.

It may be noted that the temperature at which a steel loses all the hardness which it has acquired by quenching agrees very approximately with that at which it loses any hardness acquired by overstrain.

Summary.—The conclusions arrived at in the present paper may be summarized as follows:—

The hard structure which can be produced in carbon steels by quenching and in certain alloy steels by normal cooling, is due to the presence of a hard amorphous solution of α iron and iron carbide, which solution may be compared to Beilby's amorphous phase formed by overstrain.

To explain the formation of this amorphous phase the author advances a theory that the passage of a substance from one allotropic modification to another of different crystalline form involves the temporary formation of an amorphous state, corresponding to the liquid phase of the modification about to be formed. In iron such a change occurs at Ar_1; and if, due to sudden cooling or to the presence of certain alloyed elements, the change-point is lowered to a temperature below that at which crystallization in the viscous mass becomes difficult, then the amorphous form will be retained in a metastable form in the cold.

The influence of carbon in enabling a hard amorphous structure to be retained by quenching is twofold, viz. :—

(1) As above, by its action in lowering the temperature of the change point ; and

(2) In a more essential manner, by the fact that—owing to their mutual insolubility in the solid state—segregation movements of both the α iron and the iron carbide molecules must take place in the amorphous solution formed at Ar_3, before either can assume a crystalline formation.

REFERENCES.

[1] Rosenhain and Ewen : "Intercrystalline Cohesion in Metals," *Journal of the Inst. of Metals*, No. 2, 1912, vol. viii.

[2] Rosenhain and Ewen : "Intercrystalline Cohesion of Metals," second paper, *Journal of the Inst. of Metals*, No. 2, 1913, vol. x.

[3] Rosenhain and Humfrey : "The Tenacity, Deformation, and Fracture of Soft Steel at High Temperatures," *Journal of the Iron and Steel Inst.*, 1913, No. 1.

[4] Humfrey : "The Influence of Intercrystalline Cohesion upon the Mechanical Properties of Metals," Iron and Steel Inst., *Carnegie Memoirs*, 1913.

[5] Humfrey : "The Intercrystalline Fracture of Iron and Steel," Iron and Steel Inst., *Carnegie Memoirs*, 1913.

[6] Campbell and Haskins : "Effects of Heat Treatment on the Colorimetric Test for Carbon in 0·32 per cent. Carbon Steel," *Journal of the Iron and Steel Inst.*, 1913, No. 2.

[7] Goerens : "On the Influence of Cold Working on the Properties of Iron and Steel," Iron and Steel Inst., *Carnegie Memoirs*, 1911.

[8] Rosenhain : "Recent Advances in the Metallography of Steel," Staffordshire Iron and Steel Inst., 1910.

[9] Benedicks : "The Cooling Power of Quenching Velocities, etc.," *Journal of the Iron and Steel Inst.*, 1908, No. 2.

[10] Grenet : "The Transformations of Steel within the Limits of the Temperatures Employed in Heat Treatment," *Journal of the Iron and Steel Inst.*, 1911, No. 2.

[11] Carpenter, Hadfield, and Longmuir : "On the Properties of a Series of Iron-Nickel-Manganese-Carbon Alloys," Seventh Report of the Alloys Research Committee, Institute of Mechanical Engineers, November 17, 1905.

[12] Rosenhain : "Deformation and Fracture of Iron and Steel" *Journal of the Iron and Steel Inst.*, 1906, No. 2.

THE HARDENING OF METALS BY QUENCHING.

Professor C. A. Edwards, D.Sc. (Manchester), read a Paper on "The Hardening of Metals by Quenching."

It is well known that steels are not the only metals which are capable of being hardened by the simple operation of quenching from moderately high temperatures. The degree of hardening attained after subjecting steel to this treatment is certainly much greater than in the case of other alloys, but that fact alone is not sufficient reason for invoking any special allotropic state or condition which is not possessed by other alloys.

All that is necessary is to state the simple fact, that steels are the higher members of a group of different alloys which possess the same general characteristics in varying degrees.

All alloys which behave in this way have similar constitutions at high temperatures and undergo precisely similar changes as they cool to the temperature of the atmosphere. They undergo decomposition at certain critical temperatures during which evolutions of heat occur. It is generally admitted that the hardening produced by quenching any of these alloys is in some way related to the effect of the quick cooling upon those critical heat changes.

Only when we come to consider in detail what that effect is are we faced with any divergence of opinion. Within certain limits, the effect of varying rates of cooling upon the carbide change and other similar changes is well known. For example, as the rate of cooling is increased the temperature at which those changes occur is progressively lowered, and at the same time the thermal magnitude or intensity is decreased. Therefore, it is certainly in agreement with actual experimental facts to say that as the rate of cooling is increased there is an increased tendency to prevent the inversion and keep the heat of the carbide change inside the cold material. The crucial question is, are the highest rates of cooling we are able to obtain by quenching sufficient to completely suppress the heat change? The very careful experiments that Professor Benedicks has made certainly indicate that when the highest quenching velocities are attained there are no indications of any heat being evolved as a result of the decomposition of the initial solid solution and subsequent crystallization of fresh constituents. Further, when heat is evolved the specimens contain the constituent known as troostite. There are, therefore, very good reasons for saying that troostite is the first constitutional step in the breaking up of the previous solid solution. Whilst troostite is unquestionably a hard constituent it is not nearly so hard as the constituent from which it is formed. Hence these facts lead one to the view that the hardening is caused by the suppression of the heat of the carbide inversion. In the opinion of some investigators the structures of

quenched steels do not seem to support this view. It is, therefore, necessary to consider this question very carefully, especially as all other supposed difficulties will automatically disappear once this is satisfactorily settled. There can be no doubt that the internal microstructure of steels and of other similar alloys when at high temperatures is essentially the same as that of pure metals and ordinary solid solutions, i.e. they consist of ordinary crystals with polygonal boundaries. In ordinary steels which have been quenched that kind of structure is never obtained, but an interlacing network of needles which is called martensite is always formed. On that account it has been generally assumed that the original solid solution has undergone at least a partial decomposition and its constituents have become separated into their own particular crystalline form. It ought to be remembered that differences of structure of this kind do not necessarily indicate a real difference in physicochemical constitution, because exactly the same effect can be produced in a perfectly pure metal. When these differences are observed in a pure metal, it is a sign that the crystals with the acicular markings have been strained, and if the straining has been produced under suitable conditions the metal is generally made harder.

The view which Professor Carpenter and the writer have advanced is that in the operation of quenching the normal heat of the carbide, or other similar change, is retained in the rapidly cooled material, and when the heat change is suppressed in this way very severe internal stresses are set up, and these cause internal straining of the material. That the material is internally strained is evident from the facts which have been published, namely, the metallic crystals are broken up into an exceedingly large number of twin lamellæ. Further, we believe that the hardness produced by quenching is brought about by crystal twinning and possibly direct slipping, and the formation of amorphous layers as a result of the internal deformation.

In disagreement with this theory Dr. Rosenhain says: "This view meets with the insuperable difficulty that although quenching does set up severe stresses in steels it does not cause any serious flow or movement. The strain hardening of metals only becomes marked when severe plastic flow has occurred; it was large strains that were required, that was, the actual linear displacement of particles of matter within the mass had to be large." The above is no doubt a correct statement of facts when applied to certain cases and under certain defined conditions such as direct tensional straining. It is, however, rather important to remember that the ratio of stresses to strains, and their quantitative effect upon the hardening of metals, varies within exceedingly wide limits even in the same metals, under different conditions. Hence the terms "very severe straining" and "large linear displacement" do not seem to have any tangible meaning; their effects upon the hardening of metals are materially influenced by the two factors, time and temperature. There are also good grounds for considering that the effects of compression stresses and strains upon hardening are quite different in degree from tensional stresses and strains.

Thus Hanriot has shown that by simply subjecting cylinders of silver to uniform pressures of 10,000 kilogrammes per square centimetre the hardness is increased from 1·0 to 1·7. This hardening is brought about without any apparent deformation or change of shape.

Then, remembering that steels in the γ condition are capable of forming twin crystals, it is not surprising that in the quenching operation large numbers of twin lamellæ are formed. This crystal twinning is a definite indication of internal movement.

Mr. Humfrey's theory of hardening is not much unlike the one advanced

by Professor Carpenter and the writer. In both theories the hardness is considered to be due to the presence of amorphous material. Hence it is only a question of how that material is brought into existence. Considering that the formation of an amorphous condition from a previous crystalline state must involve an actual absorption of energy, it is not easy to understand how that energy can be supplied from the interior of a slowly cooling mass of material, as Mr. Humfrey supposes. In other words, it does not seem theoretically possible, nor does it appear necessary to suppose, that, in passing from one allotropic modification to another, crystals must revert to the amorphous state. On the other hand, when crystal twinning occurs as a result of quenching stresses, energy is absorbed and may be stored up in the amorphous layers. Thus it appears to the writer that the amorphous phase cannot be formed without some internal movement. This difficulty is completely overcome if it is admitted that twinning takes place.

Turning now to the note at the end of Dr. Desch's paper, the writer would like to say that the facts brought forward by that author are not opposed to the theory of hardening by twinning and possibly direct slipping. It should be remembered that the Widmanstätten structure seen in slowly cooled carbon steels is not composed of twinned crystals, and therefore the fact that they are soft cannot be regarded as having bearing upon the theory of hardening metals by crystal twinning which is produced by quenching. It may be that the ferrite of steels containing about 0·5 per cent. of carbon is deposited and continues to grow at the twinning or gliding planes, but that is not a proof that actual twinning takes place during slow cooling. Then again, so far as the writer is aware, the Widmanstätten structure has never been observed in a steel of the eutectoid composition. This seems to indicate that the Widmanstätten structure which is developed in slowly cooled steels, with lower carbon content, is caused by the gradual growth of the ferrite. When steels are quenched from high temperatures the crystals are undoubtedly twinned. A severely twinned metal is much harder than the same material in the undisturbed condition ; in fact, this is the foundation upon which Tammann builds his theory of hardening by the cold working of metals. Of course, the presence of a relatively small number of twin crystals such as exist in annealed brasses does not materially affect the hardness of the mass, but exactly the same applies to the direct slipping upon a few gliding planes produced by slight deformation.

THE HARDNESS OF SOLID SOLUTIONS.

Dr. Cecil H. Desch (Glasgow) presented a Paper on "The Hardness of Solid Solutions," which was communicated by **Dr. T. Martin Lowry, F.R.S.**

Most of the recent contributions to the subject of the hardness of metals have dealt with the hardening produced by quenching, by cold-working, or by surface flow. A complete theory of hardening must, however, also take into account the facts relating to the hardness of solid solutions (mixed crystals). It is well known that the hardness of the alloys of a pair of completely isomorphous metals, such as gold and silver, is not an additive property, but is always greater than the hardness calculated by the rule of mixtures. For example, in the instance just mentioned an alloy containing equal weights of gold and silver is about twice as hard as either of the component metals, and alloys of gold and copper, or of copper and nickel, present similar maxima in the curve of hardness. When the two metals form a compound which enters into solid solution with both of its components, the curve of hardness presents a downward-directed cusp at the composition of the compound, with a maximum on each side. This case is very clearly exemplified by the remarkable alloys of cadmium and magnesium,* the cusp corresponding with the compound MgCd. The same conditions may be traced, although complicated by other factors, in the alloys of copper with zinc and tin, and of silver with magnesium.

The hardness of the elements is a periodic function of the atomic weight, the curve of hardness bearing a close resemblance to the curve of atomic volume. Benedicks found that the hardness is closely proportional to the atomic concentration, that is, the number of atoms in unit volume, expressed by the quotient of the density by the atomic weight, and the rule has been extended to compounds by employing the mean atomic weight (molecular weight divided by the number of atoms in the molecule). A very close agreement is not to be expected, in view of the numerous sources of error in determining the relative hardness of different solids. It has been shown † that the most considerable deviations are found in substances which exhibit very perfect cleavage, and therefore yield to an abnormal extent when submitted to the usual methods of testing.

A closer agreement between theoretical and experimental values for the hardness has been obtained by the application of Van der Waals' equation to solids.‡ In the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

* G. G. Urazoff, *Zeitsch. anorg. Chem.*, 1911, **73**, 31.

† J. L. C. Schroeder v. d. Kolk, *Proc. k. Akad. Wetensch., Amsterdam*, 1901, **3**, 655.

‡ I. Traube, *Ber.*, 1909, **42**, 1594 ; *Zeitsch. anorg. Chem.*, 1903, **34**, 413 ; 1904, **40**, 372 ; C. Benedicks, ibid., 1905, **47**, 455. See also G. Tammann, *Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen*, Leipzig, 1907, p. 31.

$\frac{a}{v^2}$ is termed the internal pressure, and an arrangement of the elements in order of their internal pressure coincides almost completely with the order of hardness. This is illustrated by the following figures, extracted from a table given by Traube, to which the values of the atomic concentration have been added :

Element.	Atomic Concentration.	Internal Pressure (Megabars).
Potassium	0·022	8,190
Sodium	0·042	18,500
Lead	0·055	51,500
Tin	0·061	68,700
Copper	0·140	236,100
Nickel	0·151	306,300
Carbon (diamond)	0·290	5,458,000

On both of these views, the increased hardness of solid solutions is due to an increase of pressure, regarded by Benedicks as osmotic pressure and by Traube as internal pressure in the above sense. Benedicks has calculated the osmotic pressure due to dissolved carbide in a quenched steel containing 0·89 per cent. of carbon to be 137·8 atmospheres, assuming the carbide molecule to be Fe_3C, or 68·9 atmospheres, assuming it to be Fe_6C_2.

These relations make it clear that the problem of hardness is connected with that of the close packing of the atoms or molecules in a solid. Different views have been taken as to the nature of the packing in the metals. According to Barlow and Pope* those metals which crystallize in the regular system are represented by the cubic closest-packed assemblage of equal spheres. "It must not, however, be concluded that for this reason all the spheres composing the structure are identically treated in the packed assemblage ; some, selected homogeneously, might be differently treated from others and the assemblage yet exhibit holohedral, hemihedral, or tetartohedral symmetry of the cubic system according to the particular type of homogeneous distribution of the preferentially treated spheres."

In the simplest cubic arrangement, each sphere is in contact with twelve others, and compression continued until the intervening spaces are completely obliterated converts each sphere into a regular rhombic dodecahedron. On the other hand, Sollas† assumes comparatively loose packing of the component spheres.

It has recently been found possible to apply an experimental test. The discovery that the reflection of X-rays by crystals bears an intimate relation to the internal structure of the crystal provides a means of investigating this structure. So far only one metal has been examined in this way. Crystals of native copper, when submitted to the action of X-rays, reflect the latter at certain angles, indicating that the unit of the space-lattice for this metal is the face-centred cube.‡ This structure corresponds with the simple closest-packed cubic arrangement, in which every atom, regarded as a sphere or parallelohedron, is in contact with twelve similar spheres or parallelohedra. Whether closest-packing is absolutely essential to the interpretation of the

* *Trans. Chem. Soc.*, 1907, **91**, 1150.
† *Proc. Roy. Soc.*, 1898, **63**, 270 ; 1908, **80A**, 267.
‡ W. L. Bragg, *Phil. Mag.*, 1914 [vi], **28**, 355.

experimental results is, however, not quite clear, and the opinion of an expert crystallographer on this point would be of interest.

There are many types of crystalline solid solution, and it will be advisable to consider only the simplest of these at present. The most important pairs of metals which form complete series of solid solutions with one another are: gold-silver, gold-copper, copper-manganese, copper-nickel, gold-platinum, platinum-iridium, and antimony-bismuth. All but the last of these pairs crystallize in the cubic system. The pair magnesium-cadmium may be omitted on account of the complication introduced by the compound MgCd. This leaves six pairs which are fairly well known, and of which the members crystallize in similar simple forms. In each case, the two components have nearly equal atomic volumes; and these volumes are small, gold, silver, copper, manganese, nickel, and the platinum metals all occurring at or near the minima on the periodic curve of atomic volumes. The following values may be adopted:

Au	...	10·202	Ni	...	6·64
Ag	...	10·233	Pt	...	9·06
Cu	...	7·077	Ir	...	8·61
Mn	...	7·44			

The case of the alloys of gold and silver may be regarded as typical. The atomic volumes of the two metals are very closely similar. The internal crystalline arrangement of silver and gold has not yet been determined by the method employed for copper, but the external crystallographic characters are almost identical, and it is probable that an exactly similar space-lattice will be found to fulfil the conditions of all three metals. The difference between the atoms of gold and silver is then so small that the two space-lattices should interpenetrate freely without appreciable distortion, and the solid solutions of the two metals should be crystallographically indistinguishable from their components. The available data are too scanty to decide whether this is actually the case. The native alloy, electrum, is described as similar. It is hoped that an examination of the alloys by the X-ray method may shortly be undertaken. The fact that the freezing-point and solidus curves of the gold-silver system approach so closely to a straight line also suggests that the mixture is of a very simple type, whilst the specific volume is strictly proportional to the concentration, the greatest deviation from the mixture rule being only + 0·2 per cent. Diffusion of silver into gold takes place very readily; for example, a gold wire, 0·46 mm. in diameter, was coated electrolytically with silver until the compound wire contained 62·7 per cent. Ag. The electrical conductivity was determined, and the wire was then heated at 900°. The conductivity gradually fell, and reached a final value after 120 hours. The diameter of the wire was then 0·98 mm., and its conductivity was that of a homogeneous alloy of the same dimensions and composition.*

These facts indicate that the solid solutions of gold and silver are of a very simple character. Nevertheless, the hardness of the alloys is considerable, attaining a maximum value which is twice that of the pure metals, whilst the electrical conductivity is correspondingly diminished, passing through a minimum. Of the two explanations which first suggest themselves, an alteration in the closeness of packing seems improbable in view of the equality of the atomic volumes throughout the alloys. There remains the assumption of a condition of internal strain. On this view, the hardness

* G. Bruni and D. Meneghini, *International Journal of Metallography*, 1912, **2**, 26.

of a solid solution is due to the same cause as that of a cold-worked metal, namely a disturbance of the crystalline structure, giving rise to an amorphous or irregular arrangement of the atoms or molecules, or at least, if the conditions be regarded from a kinetic point of view, to a constraint of the atomic or molecular motions. This is an aspect of the problem which has been treated by Dr. Beilby, but has received very little attention from other writers.

According to Tammann,* the increased hardness of solid solutions is due to the fact that "the attractive force between two different molecules is always greater than the attractive force between two similar molecules in the same mixture." It is therefore to be expected that the attraction, and consequently the hardness, should be a maximum in the solid solution containing equal molecular proportions of the two components, and this rule is approximately fulfilled in the case of several of the series investigated by Kurnakoff and Schemtschuschny.† It may be noted that the rule is confirmed by application to cases in which an intermetallic compound is formed. Thus, the compound MgCd forms a continuous series of solid solutions with both of its components. The maximum hardness is not that of the compound, although this is harder than either component, but the curve plotted with atomic percentages presents two maxima, approximately midway between Mg and MgCd and between MgCd and Cd respectively. These are the two compositions at which there is the greatest admixture of foreign molecules.

Direct evidence of a constrained condition of the molecules of a solid solution, or of a disturbance of the internal crystalline structure, is not easy to obtain in the case of metals, but the conditions are more favourable in that of isomorphous salts. These salts frequently exhibit "optical anomalies," indicating the presence of internal strain, and such a condition is often assumed to be usual. It is, however, by no means necessarily the case. In his very careful work on isomorphism, Retgers‡ has shown that the anomalies do not always occur, and has used their absence as one of the tests of the homogeneity of isomorphous "mixed crystals" required for investigations of density. The most conspicuous examples of crystals exhibiting optical anomalies are those of salts crystallizing from solutions containing dyes. Here there is no question of the interpenetration of space-lattices, and the production of a strain in the crystals is readily comprehensible, but where two salts of almost identical molecular volume are concerned, it seems probable that Retgers' view is correct, and that optical anomalies are absent when sufficient care is taken to conduct the crystallization slowly and in presence of a large excess of the saturated solution.

It is usually stated, also, that solid solutions crystallize less readily, or yield less perfect crystals, than pure substances. This is not invariably the case, but the fact has been observed so frequently that it must be regarded as evidence for a certain disturbance of crystalline structure in solid solutions.

The heat of formation of solid solutions has hitherto been determined only in the case of isomorphous salts, and then by an indirect method, the heat of solution of the solid solution in water being compared with that of a mechanical mixture of the components in the same proportions. The pairs of salts which have been examined satisfactorily by this method—NaCl–KCl, NaBr–KBr, NaI–KI, KCl–RbCl, KCl–KBr, KBr–KI, KCl–KI, $NaNO_2$–$NaNO_3$

* *Lehrbuch der Metallographie*, Leipzig, 1914, p. 332.
† *Zeitsch. anorg. Chem.*, 1908, **60**, 1.
‡ *Zeitsch. physikal. Chem.*, 1889, **3**, 497.

—all give results indicating a negative heat of formation for the solid solution.* For two of these pairs, namely KCl–KBr, and KBr–KI, the hardness curve, as determined by measuring the pressure required to produce flow through an orifice, passes through a maximum not far from the middle of the series.†

It will be seen that the data which are available for drawing a conclusion as to the hardness of solid solutions, even in such a simple case as the alloys of gold and silver, are very scanty. The complete proportionality which exists between density and composition by volume (or between specific volume and composition by weight) seems to exclude any important differences in the closeness of packing. There remains a difference in the attractive forces between the atoms—what is usually called internal pressure, and even here it is not easy to realize why the attractive force between gold and silver should be twice as great as between gold and gold or between silver and silver. A distortion of the space-lattice, producing a more or less irregular arrangement, is only compatible with the conservation of the original density on the assumption of some form of packing which is not the closest possible. It would therefore seem that the solution of the problem must be sought from the crystallographers, whose newly added resources enable them to determine the direction of the planes of closest packing within a crystal, and the actual form of the space-lattice.

NOTE ON CRYSTAL TWINNING AND THE MARTENSITIC STRUCTURE.

Dr. Cecil H. Desch also contributed a "Note on Crystal Twinning and the Martensitic Structure."

The present note deals with certain points in the paper communicated to the Spring Meeting of the Iron and Steel Institute by Professors Edwards and Carpenter, and with some experiments undertaken as a result of the discussion on that paper. One of the conclusions drawn by the authors on that occasion was that martensite and austenite were constitutionally identical, and differed only in the repeatedly twinned structure of the former. The hardness of martensite was attributed to the formation of amorphous material at the surfaces of slip on which twinning occurs. The so-called "acicular" structure of certain quenched aluminium-copper alloys was also regarded as due only to twinning. The structure of these alloys is distinctly "martensitic," and the analogy between them and the martensitic steels is undoubtedly a close one.

It is difficult to believe that the only difference between austenite and martensite lies in the repeatedly twinned structure of the latter constituent, accompanied by the formation of amorphous material. As Professor Benedicks and Dr. Stead, among others, have pointed out, distinct differences are observable in the behaviour of the two constituents when present together in the same specimen of steel, and in the change of volume which occurs when austenite is cooled in liquid air. Hannemann has also shown reason for believing that austenite and martensite behave differently when resolved by tempering.

The present writer has never accepted the hypothesis of a hard modification of iron, and has always regarded the hardness of martensite as being connected with a partial resolution of austenite. That the resolution should

* G. Bruni, *Mem. R. Accad. Lincei*, 1912, p. 50.
† T. B. Vrshesnevsky, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1364.

proceed along gliding and twinning planes by preference is only in accordance with the usual behaviour of solid solutions, as evidenced by the formation of the Widmanstätten structure when such solid solutions undergo partial resolution,* and by the fact that corrosion proceeds preferentially along twinning planes.†

Narrow twins (Neumann's lines) are readily developed in many metals. Professors Edwards and Carpenter have instanced the case of tin. Bismuth is also a convenient material for exhibiting the effect. Fig. 1 shows a portion of a crystal grain in a small ingot of cast bismuth, every grain of which is traversed by numerous Neumann's lines, as well as by broader and less regular twin lamellæ. In cast zinc the lines may be so closely packed and so narrow as to simulate very closely the structure of martensite. Whether these lines owe their origin to casting strains or to strains produced in cutting and filing the ingot is not decided, and there is no evidence that the abundance of very narrow twin lamellæ is accompanied by increased hardness.

The presence of a martensitic structure without increase of hardness is illustrated by Figs. 2, 3, and 4, which represent fields from a piece of overheated steel. A piece of steel plate, 0·28 per cent. C, was heated to a white heat in a coke fire and allowed to cool down with the furnace. A very coarse structure, like the Widmanstätten structure but with less regular outlines, was developed. The ferrite cell-walls were fringed with ferrite (Fig. 3) and the pearlite areas exhibited a remarkable pseudo-martensitic structure (Figs. 2 and 3) which had all the appearance of coarse martensite. Tested with a needle it proved to be quite soft, as might have been expected from the very slow cooling. Examined with an immersion objective the whole mass proved to be made up of pearlite (Fig. 4), closely packed in some parts and more loosely in others.

Such a structure may, of course, be regarded as pseudomorphic after martensite, but it is impossible for the martensitic structure to have been produced by anything of the nature of chilling. The writer is inclined to take the view that resolution of the original austenite takes place most readily along gliding and twinning planes, and that the distribution of the pearlite in the slowly cooled specimen records the earlier stages of the resolution. On this view, the martensitic structure of a quenched steel is an accompaniment, and not the cause, of its hardness. The writer is aware that this suggestion does not provide any explanation of the hardness of martensite, but only opposes the view that that hardness is due to twinning. Martensite is so much harder than its components as to suggest the presence of a solid solution, but whether that solid solution be a distinct phase, not yet recorded in the equilibrium diagram, or an unusual type of highly strained solid emulsion, remains doubtful.

The investigation of the distribution of pearlite in a slowly-cooled steel is being continued.

* See paper by N. T. Belaiew in *J. Inst. Metals*, 1914, vol. 12, and discussion.
† S. Whyte and C. H. Desch, ibid., 1914, **11**, 235.

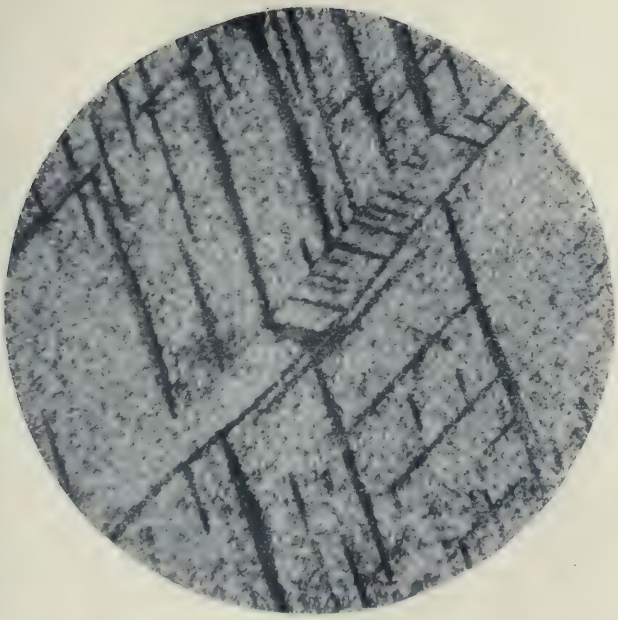


FIG. 1.—Twinning in Cast Bismuth.

FIG. 2.—Martensitic Structure in slowly cooled Pearlite.

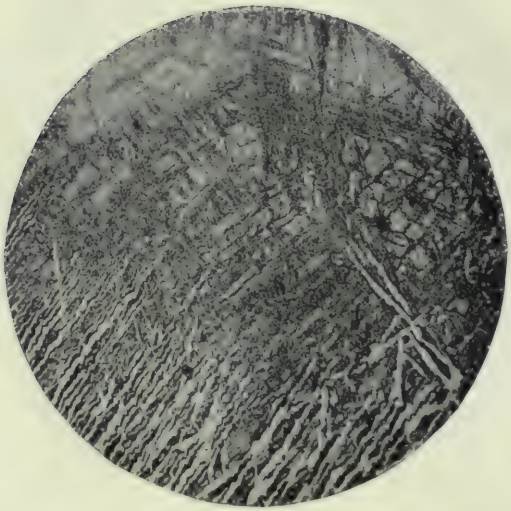


FIG. 3.—Ferrite Fringe and Pearlite showing Martensitic Structure.

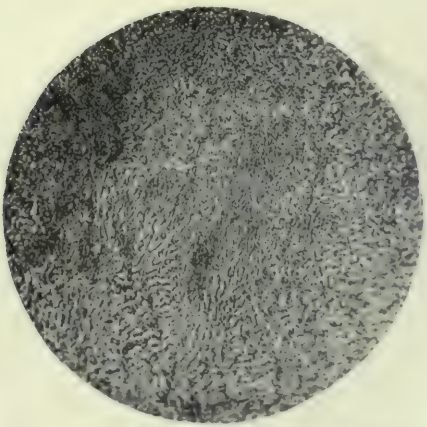


FIG. 4.—Pearlite in same specimen with 2 mm. Objective of 1·4 NA.

THE INTERSTRAIN THEORY OF HARDNESS.

Mr. Andrew McCance, A.R.S.M., B.Sc. (Glasgow), contributed a Paper on "The Interstrain Theory of Hardness," which was communicated by the Secretary.

1. There are three methods by which a pure metal may be made harder, namely, by mechanical deformation, by the addition of elements which form solid solutions, and by the application of heat treatment (in certain cases), but as yet there is no theory which can be said to demonstrate the underlying connection which must exist between these three means of achieving the same end. For it can be said with certainty that so long as the metal retains its chemical characteristics the same effects must be derived from the same immediate causes.

It is with the hardening effect caused by heat treatment that this short paper will deal, but it can be shown that what is true for iron is also generally true for all alloys where corresponding conditions exist.

2. The great amount of attention which has of late been concentrated on the nature of the allotropic changes in pure iron has made it clear that from ordinary temperatures up to 1,000° C. only two real allotropic forms of iron exist, the alpha and the gamma, and that the so-called beta iron is in reality alpha iron which has become non-magnetic from purely thermal causes, the apparent liberation of heat at A_2 being due to the rapid change in the specific heat which necessarily accompanies the ferromagnetic transition.*

Since alpha iron loses its magnetic properties above a definite temperature, it might be suggested that gamma iron, which at high temperatures is non-magnetic, might itself become magnetic at lower temperatures. Non-magnetic manganese steel, however, is not transformed even at the temperature of liquid air,† and no treatment can make austenitic steels magnetic which does not increase the specific volume at the same time, and when this takes place it points conclusively to the transformation to alpha iron, for the thermal magnetic transition makes no appreciable alteration in the specific volume.

The development of enormous crystals in low carbon steels which have been strained and afterwards reheated to any temperature below Ac_3,‡ and in thin sheets of electrolytic iron cooled from above Ac_3,§ proves that iron possesses the same crystalline form above A_2 as below it, and that therefore the A_2 point is not evidence of allotropy.

3. The great and important distinction between the two forms of iron is their behaviour towards carbon, which is soluble in alpha iron only to a very

* McCance, *Four. Iron and Steel Inst.*, 1914, i., p. 223. Benedicks, *Four. Iron and Steel Inst.*, 1914, i., p. 439.

† Hadfield, *Four. Iron and Steel Inst.*, 1905, i., p. 179.

‡ Stead, *Four. Iron and Steel Inst.*, 1898, i., p. 145. Chappell, *Four. Iron and Steel Inst.*, 1914, i., p. 472.

§ Stead and Carpenter, *Four. Iron and Steel Inst.*, 1913, ii., p. 113.

small extent but can dissolve with readiness in gamma iron, and on this preferential treatment rests the explanation of the unique position which carbon occupies as a cause of hardening by quenching in iron. There is no doubt that if another element can be found which possesses the same property of exclusive solubility in gamma iron, then that element also will possess to a similar extent the hardening power of carbon.

4. Pure iron in common with all metals is hardened after permanent deformation, and it is best described after such treatment as being in a condition of "interstrain." Metals in their normal unstrained condition are crystalline. That is, they are composed of an orderly arrangement of their constituent atoms arranged in a space lattice which conforms with whatever symmetry the crystals possess. Successful attempts have been recently made by the aid of X-rays to determine the actual position occupied by the atoms, and copper,* for instance, has been shown to have its atoms built up in a "face centred" cube, that is a cube having an atom at each corner and one at the centre of each face.

The effect of deformation on such systems must be to alter the position of each atom relatively to its neighbour, and permanent deformation must cause so much alteration that the atoms along the planes of slip can no longer return to their positions of equilibrium. This corresponds to the condition of interstrain and results in a hardening of the material. That the destruction of the crystalline arrangement goes so far as to render the material in those planes of greatest movement actually amorphous and devoid of crystalline form, as Beilby has proposed, has never been seriously questioned, but the writer thinks that the following facts are strong arguments against this theory of a hard vitreous amorphous phase. In the case of a dimorphous metal like iron the vitreous phase to be truly amorphous must possess the same physical properties, no matter from which crystalline form it has been produced by deformation, and since strained alpha iron loses none of its magnetic intensity, we must assume that amorphous iron is magnetic; consequently it is to be expected that strained gamma iron will also be magnetic since the same constituent is produced. The important results of Hadfield and Hopkinson† show, however, that the magnetic intensity of austenitic manganese steel after severe straining is only augmented to 0·3 per cent. of the intensity of pure iron, and is still practically non-magnetic, although the hardness has increased from 200 to 490. It would seem that the iron in the interstrained condition has not lost the distinguishing properties which are the result of crystalline form.

Hanriot‡ exposed small cubes of metal to a fluid pressure of 10,000 kgs. per sq. cm., and although no measurable deformation could be detected, the hardness had increased in every case as follows:—

Metal.	Hardness (before).	Hardness (after).
Silver	20·3	32·2
Iron	57·7	62·3
Brass	24·0	36·5
Zinc	33·1	43·0

The microstructure was the same after this treatment as before, while to suggest that the hard vitreous phase had been formed as the result of pressure would of course be out of the question, since iron expands on

* Bragg, *Phil. Mag.*, September, 1914.
† Hadfield and Hopkinson, *Jour. Iron and Steel Inst.*, 1914, i., p. 125.
‡ Hanriot, *Comptes Rendus*, 155, pp. 713 and 1502.

becoming liquid and would have its melting-point raised and not lowered by pressure.

Deformation does not necessarily produce an amorphous constituent, but only results in some permanent alteration of the atoms from their positions of equilibrium in their crystalline space lattice; and conversely, it will be true that any metal whose atoms are prevented from reaching their positions of equilibrium will be in a condition of interstrain and will be hardened.

5. To harden steel it is necessary to heat it above the Ac_r point, that is to heat it to the temperature at which the carbon is all in solution, and then to cool it at a rate which is sufficiently rapid, but the greatest hardness is

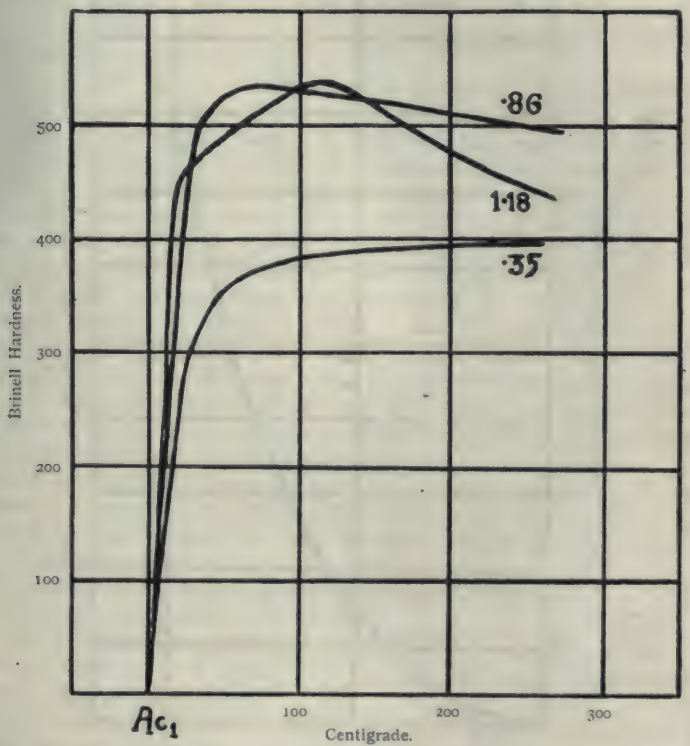


FIG. 1.—The units are degrees Centigrade above the Ac_1 point, and increase in hardness in Brinell numbers above the annealed value.

obtained when the temperature reaches the highest change point—that is the Ac_3 for hypoeutectoid and $Ac_{cementite}$ for hypereutectoid steels. This is shown in Fig. 1, giving the hardness of three steels with 0·35 per cent., 0·86 per cent., and 1·18 per cent. carbon, and the temperature of quenching in degrees above the Ac_1.

With 0·35 per cent. carbon the structure after quenching from just above the Ac_1 will consist of ferrite and martensite areas (separated by transitional troostite, etc.), and the increase in hardness from this to just above the Ac_3, when the structure is wholly martensitic, corresponds with the gradual replacement of the ferrite by the harder constituent. With 1·18 per cent.

carbon the greatest hardness is obtained by quenching from just above the $Ac_{cementite}$, and the softening which takes place on increasing the temperature corresponds with the appearance of austenite in the micro-section. A very important result is that when the carbon reaches about 0·7 per cent. a maximum hardness is obtained in the quenched state, and this value is not exceeded in any pure carbon steel. If the hardness were the direct consequence of carbon in solution, the hardness would be proportional to the amount of carbon dissolved. That it is not so shows that the action of carbon is indirect and that the hardening element is the iron itself.

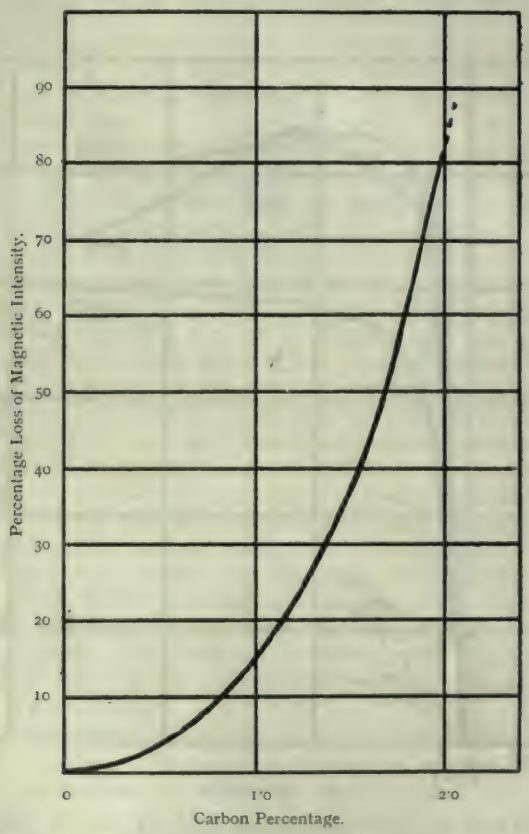


FIG. 2.—From data published by Hadfield and Hopkinson and by the author.

6. It is a fact well known that steels which at the temperature of quenching are non-magnetic, are magnetic in their hardened state, and this change must have taken place during the time occupied by the quenching. Since it has been previously shown that gamma iron does not itself become magnetic, it is necessary to conclude that during the time occupied in cooling from the higher temperature to the lower the original gamma must have changed to the magnetic alpha condition. Measurements of the electric resistance show that the carbon has not changed its condition but has remained in solution, and so we recognize the fact that under the

conditions of quenching the transformation of the iron from the gamma to the alpha state can take place independently of the change in the state of the carbon from a state of solution to the undissolved state. These two transformations, which on slow heating and cooling take place simultaneously, can behave as independent reactions, although in a sense which is limited. For though martensite may be considered as an enforced solution of carbon in alpha iron, it must not be forgotten that there is still some gamma iron present with the carbon, which is absolutely necessary to maintain its solubility, and any change in the state of the carbon causes the transformation of this gamma iron to alpha. It might on this account be suggested that the iron is chemically combined with the carbon, but an examination of the curve (Fig. 2) connecting the loss of magnetic saturation intensity with the carbon content shows that the gamma iron increases much more rapidly than the amount of carbon, which points to purely physical influences.

7. It has been shown elsewhere* that it is possible to calculate the velocity of quenching in a round bar on certain assumptions which are closely realized in the early stages, at least, of quenching, and if the curve thus obtained is compared with the curve connecting the electric resistance or the loss of magnetic intensity of a steel with 0·86 per cent. carbon, it is seen that they are closely similar, so that the amount of carbon in solution and the amount of gamma iron retained in the cold state are proportional to the rate of cooling; at least until the carbon is completely in solution.

With a given rate of cooling the progress of the transition from the equilibrium position for gamma crystals to that of alpha crystals will be arrested, and will ultimately be stopped, by the increase in the internal viscosity at the lower temperature. The crystalline transformation in other words will be partially suppressed, and a condition produced which is essentially similar to the condition of interstrain produced by deformation, and the hardness which results is accounted for by this condition.

During the cooling of hypoeutectoid steel from a temperature at which it consists of a homogeneous solution of carbon in gamma iron, its complete transformation into alpha iron and cementite comprises two individual transformations:

(*a*) A change in the state of the iron from gamma to alpha.

(*b*) A change in the state of the carbon.

The first of these can take place independently of the second, but when the second takes place it necessarily involves the first. Three possible conditions can therefore result.

1. Both transformations are completed: this is the normal pearlitic condition of steel, which is soft.

2. Both transformations are suppressed: this corresponds to the condition of pure austenite, which is also comparatively soft but non-magnetic.

3. When (*a*) takes place but (*b*) is suppressed—that is, the complete transformation is partially suppressed—then the structure is martensitic and the alpha iron formed under this condition is interstrained and very hard.

Case (3) then, is the important one from a hardening standpoint, and to be possible it is necessary that a difference should exist in the respective velocities of transformation of (*a*) and (*b*), so that with an appropriate rate of cooling the slower transformation can be suppressed while the faster is not greatly affected.

This intimate connection between the rate of cooling and hardening is further illustrated by the behaviour of alloy steels. The addition of manganese,

* McCance, loc. cit.

for instance, by lowering the temperature of the transformations greatly decreases the velocities with which they proceed, so that with a certain percentage (which varies with the carbon content) the transformation of the carbon may be almost completely suppressed by air cooling, and the normal condition after such treatment is martensitic accompanied by hardness and brittleness, in fact all the characteristics of quenched pure carbon steels. Water quenching, on the other hand, results in the complete suppression of *both* transformations, and the steel becomes austenitic and soft, while the same result is obtained by air cooling when the percentage of manganese is further increased.

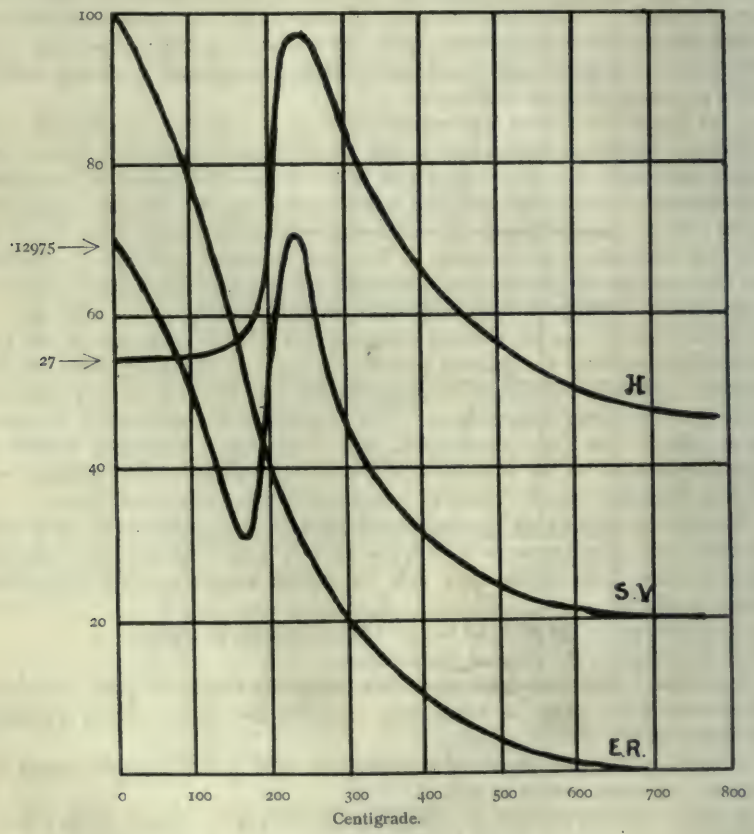


FIG. 3.—From data obtained by Maurer.

H. = Hardness curve—each vertical division represents 10 units (Shore).
E.R. = Electric Resistance—each vertical division represents 20 per cent. of the total loss.
S.V. = Specific Volume—each vertical division represents ·0004 cub. cm.

Commercial manganese steels after air cooling are non-magnetic though fairly hard and brittle, but such steels usually contain about 1·2 per cent. of carbon, and this condition is probably brought about by the deposition from a state of solution of the cementite in excess of the eutectoid composition.

Similar results are obtained by the addition of nickel, and the following facts are also instructive. A nickel steel containing 3·6 per cent. of Ni and

0·19 per cent. carbon had a normal hardness of 183, which, after quenching in water from 1,000° C., had risen to 444, but a steel containing 0·19 per cent. carbon without the nickel increased after the same treatment from 143 to 218; that is, while the plain carbon steel increased in hardness 65 points by quenching, the nickel steel increased by 259. Nickel is known not to form a carbide in this range of composition,* consequently the state of the carbon is similar in both, and the increased hardening power must be due to the influence of the nickel on the iron. It has enabled the iron to retain a greater degree of interstrain by lowering the temperature at which the transformation of the gamma to alpha iron takes place.

8. Tempering allows the metastable conditions which result from quenching to revert to their stable state. In hypoeutectoid steels the carbon is deposited from solution and the specific resistance falls, while at the same time the interstrained condition of the iron is gradually lost with the formation of alpha ferrite recognizable under the microscope.† As a consequence the magnetic permeability under low fields increases, the remanent magnetism decreases, and the peculiar shape of the curves connecting the magnetic properties with the temperature of tempering is found to be exactly similar for interstrained iron as for quenched steels—a similarity which extends also to the rate at which the hardness is lost.

Turning now to the consideration of the tempering of high carbon steels which contain a proportion of pure austenite, the curves of specific volume electric resistance, and hardness of one containing 1·66 per cent. carbon due to Maurer are given in Fig. 3.

The smooth curve for the electric resistance shows that the carbon is deposited continuously, and this causes a decrease in the specific volume, but at 150° C. to 250° C. there is a sudden increase which is without effect on the electric resistance, and must therefore be due to the transformation of gamma to alpha iron, and since this takes place independently at a low temperature under conditions of high internal viscosity, the alpha iron formed will be in a condition of interstrain and an increase in hardness should result. This is strikingly confirmed.

9. The importance of internal friction in retarding transformations and preserving the metastable state has been pointed out, and in solids this internal friction is very similar to sliding friction between solid surfaces. A fixed amount of super-cooling below the transition range, for instance, is necessary before transformation can take place in solids, and the difference in the temperature of transformation on heating and cooling is a measure of the internal friction. Twenty-five per cent. nickel steel has a transformation-point at 550° C. on heating, while on cooling it is transformed in the neighbourhood of —100° C., which shows a range of 650°; but manganese steel containing about 14 per cent. Mn has a larger difference in this respect than any other, since on heating the Ac_1 point occurs about 550° C. while the Ar_1 does not even take place at the temperature of liquid air, a range of more than 740 degrees.

Many of the abnormal properties which manganese steel possesses are due to this great friction. Deformation renders non-magnetic nickel steel magnetic through the transformation of the gamma iron to alpha with a decrease in density, but manganese steel, on the other hand, is practically unaffected magnetically.

Tempering at a temperature just below its change-point results in the

* Arnold and Read, *Engineering*, 1914, pp. 463 and 468.
† McCance, *Journ. Mechan. Eng.*, 1910, p. 1064.
‡ Maurer, *Rev. de Mét.*, 1908, p. 711.

gradual conversion of the gamma iron to alpha, and the deposition of the carbon from solution, but the alpha iron is interstrained and the hardness is increased. It is conceivable that very prolonged tempering would cause this hardness to be lost again with the production of a soft manganese steel which is magnetic.

10. When pure austenite formed by quenching 2 per cent. manganese steels or the austenite of high carbon steels is immersed in liquid air, the greater super-cooling overcomes the internal friction and the gamma to alpha transformation takes place although the carbon change is unaffected. The electric resistance is not appreciably changed, but the specific volume increases as well as the hardness, through the production of interstrained alpha iron. Maurer obtained the following results:—

Composition.	Elect. Res.	Specif. Volume.	Hardness.	Magnet. Reman.	Treatment.
Per cent.				cm.	
1·66 C	1·00	·12964	28	14·5	Quenched from 1,100° C. in iced brine
	1·04	·13105	38	28·5	Quenched from 1,100° C., immersed in liquid air
1·94 C, 2·24 Mn	1·00	·13233	17	0·8	Quenched from 1,200° C. in iced brine
	1·07	·13439	29	8·2	Quenched from 1,200° C., immersed in liquid air

11. The theory outlined above accounts for the many widely differing conditions which steel can assume as the result of heat treatment, in a manner which is simple and consistent.

It is agreed that hardening by deformation results from purely structural causes which affect the crystalline state, and there is much to recommend the term "interstrain" to describe such a condition of hardness, since it is a word which is non-committal regarding any proposed explanation of the effect. The theory of interstrain action is itself an inquiry, but it is secondary to the main issue in the hardening of steel.

HARDENING WITH AND WITHOUT MARTENSITIZATION.

Professor Henry M. Howe (Columbia University) contributed to the Discussion some remarks on "Hardening With and Without Martensitization," which were communicated by the **President.**

I would emphasize one specific way of hardening steel, which differs from all but one of the others in lacking martensitization.

The martensitizing ways of hardening are (1) that of carbon steel by rapid cooling; (2) that of steels with an intermediate proportion of manganese or nickel by air or other moderately slow cooling; (3) that of Maurer's austenitic manganese steel by cautious reheating; (4) that of 25 per cent. nickel steel by liquid-air cooling.

In addition (5) cold deformation of any ductile metal hardens it. This way of hardening in the case of manganiferous and nickeliferous austenite (Hadfield's manganese steel and 25 per cent. nickel steel) is accompanied by the acquisition of ferro-magnetism.

The non-martensitizing way of hardening (6), which I emphasize, is holding manganiferous austenite shortly below the transformation range, whether the cooling thence be fast or slow.

Of these all but (6) can be explained by the amorphous theory; it is not yet clear that (6) can.

The *Amorphous Theory* of the hardening of steel by rapid cooling refers it to the presence of a very great proportion of iron made amorphous by the formation of innumerable slip bands,* caused by the sudden expansion due to the starting of the gamma-alpha transformation at innumerable nuclei, and its arrest by the pressure thus caused. The surface of each of the innumerable particles which do transform must needs move relatively to the surface of its minute abutting neighbours, which, less prompt to start transforming, are prevented from starting thereafter by the pressure caused by the transformation and hence expansion of their prompter neighbours, pressure always tending to prevent any transformation accompanied by expansion. Only the prompter particles can transform; the tardiness of the tardy causes their transformation to be blocked by the prior expansion of the prompt.

This relative movement causes slip, and the innumerableness of the nuclei, and hence the intimacy of the mixture of the more prompt and transforming with the less prompt and untransforming particles, cause an enormous total quantity of slip, and a corresponding enormous total

* More probably slip bands than twins. Twinning as such need not harden, because the two halves of every twin should dovetail perfectly, with no ungeometrical gussets incapable of being filled by the necessarily geometrically shaped crystalline particles. During slip the slipping particles must be de-crystallized; during twinning they need not be. Witness the unlessened brightness of the twinned face of Baumhauer's artificially twinned calcite crystal.

quantity of amorphous iron, and hence in fine very great hardness.* The hardness exceeds that developed in the usual cold deformation of any metallic mass by wire-drawing, etc., because slip in this latter occurs along a relatively small number of internal surfaces, and rupture occurs and prevents further deformation as soon as the supply of crystalline metal fails along some one internal surface unfavourably disposed towards the stresses from without. This explains why it has thus far been impossible to increase the hardness of Hadfield's manganese steel beyond 550 of Brinell's scale by cold deformation.† The extent of the internal surfaces along which amorphization can be induced by mechanical cold deformation is much less than that of those along which it is caused in quenching.

The great proportion of iron thus de-crystallized in quenching remains amorphous because the temperature at which the de-crystallizing occurs is too low to permit re-crystallization, or to permit it rapidly.

The essential conditions here are (1) the innumerableness of the nuclei where transformation starts, innumerable because of the under-cooling due to the rapid cooling; (2) the low temperature of the transformation, preventing re-crystallization.

The amorphous iron explains the hardness; the alpha state of the prompter particles which have transformed explains the ferro-magnetism; the presence of untransformed gamma explains the increase of electric resistance; the intimate interlocking of the magnetic alpha with the inert gamma explains the retentivity. The martensitization tallies with the conception of the minuteness of the heterogeneousness.

This theory explains more or less readily cases (2), (3), and (4), because in each of these the transformation occurs at a temperature low enough to explain why the metal made amorphous by the internal slip does not re-crystallize. Moreover, the martensitization which occurs in each of these cases tallies with the conception of innumerable slippings.

This theory of course explains in Beilby's way the strengthening and embrittlement caused by mechanical cold deformation. It also explains the martensitization, the embrittlement, and the magnetization of austenitic steels by cold deformation. This causes local tension at many internal surfaces, and this tension, by inciting the expansion which accompanies the transformation, causes the transformation to occur at these innumerable surfaces. Hence the alpha iron and the magnetism. The tension further causes slip, and this in turn de-crystallizes the abutting metal, and thereby hardens, embrittles, and martensitizes it.

(6) But if Hadfield's manganese steel is held long at temperatures below the transformation range, e.g. at 550°, it is found to be hard after cooling, and its hardness is independent of the rate of cooling, as shown in the follow-

* The objection raised that the movement, or strain, is too slight, e.g. in the hardening of a needle, to explain the creation of enough amorphous iron to explain the hardening, breaks down on examination. It is true that in cold-working a metallic block a large degree of strain is needed to generate a large degree of hardness, and hence by inference a large proportion of amorphous iron, and that in a needle no such quantity of strain can exist, the total distances available being too small.

But this is fallacious. In cold-working a metallic block, the direction of the strains is constant throughout the mass, so that the strains are additive, and result in a great change of outer dimensions. They have a great resultant. But the strains in the postulated slips in the hardening by ways (1) to (4) are not in constant but in opposite directions along different internal micro-surfaces, and they therefore offset each other and yield no great resultant deformation of the mass as a whole.

† Hadfield and Hopkinson, *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 114.

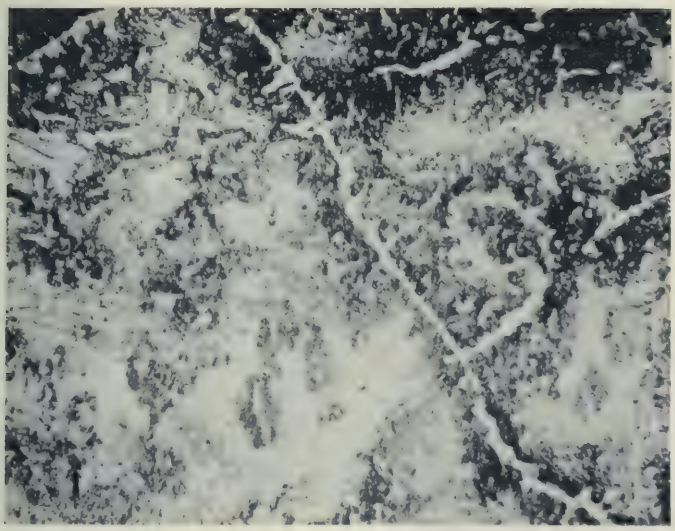


FIG. 1.—Steel of 12·80 per cent. of Manganese and 1·24 of Carbon, quenched from 1,100°, held two hours at 575°, and again quenched. Etched with alcoholic nitric acid. × 180.

FIG. 2.—Steel of 0·02 per cent. Carbon, etched with hydrochloric acid at 850°. × 500.

ing table. Moreover it is not martensitic.* I do not thus far see how the amorphous theory can explain this hardening, because at this high temperature any iron made amorphous ought to be able to re-crystallize, unless indeed it should be true that manganese includes under its general sluggardizing effect sluggishness to re-crystallize even at 550°, or that this hardening is due to the precipitation of pro-eutectoid cementite during the stay at 550°. I am about to test this last point by treating carbon-free manganese steel.

TABLE I.

Influence of the Rate of Cooling on the Hardness of Hadfield's Manganese Steel after a Sojourn at various High Temperatures.

Specimens from 3 to 23 inclusive were held at 1,100° and quenched before the treatment here recorded.

No.	Treatment. Holding Temperature, °C.	Time held, Hours.	Cooling.	Brinell Hardness. Individual Determinations.	Averages.	Structure.
1	As received		(cast + sand-cooled)	—	190	Austenite + cementite network
2	1,100	2	Quenched (in water)	—	170	Austenite
3	800	2	"	255	245	do.
4	"	"	"	235		
5	"	"	Furnace cooled	302	302	Austenite + cementite globules
6	"	"	" "	302		
7	600	0	" "	—	207	Austenite
8	550	2	Quenched	~~444~~	444	? + pro-eutectoid cementite needles
9	"	"	"	444		
10	"	"	Furnace cooled	370	372·5	do. do.
11	"	"	" "	375		
12	"	42	Quenched	~~444~~	~~444~~	do. do.
13	"	"	"	444		
14	"	"	Furnace cooled	444	444	do. do.
15	"	"	" "	~~444~~		
16	400	2	Quenched	223	235	Austenite
17	"	"	"	262		
18	"	"	"	228		
19	"	"	"	228		
20	"	"	Furnace cooled	228	241	do.
21	"	"	" "	277		
22	"	"	" "	217		
23	"	"	" "	241		

* The structure of such manganese steels after these hardening holdings below the transformation range has been reported to be martensitic, but this I believe is an error. Such steels often contain needles which indeed suggest martensite, but these needles blacken with sodium picrate, and therefore are of manganiferous cementite, and not of martensite. Moreover, in many fields these needles are replaced almost completely by a thick network separating the meshes, and closely like the pre-eutectoid cementite network in other hyper-eutectoid steels. Fig. 1 shows the structure of a specimen of this steel quenched from 1,100° and then held for two hours at 575° and quenched in water. Here the pro-eutectoid cementite is massed in the grain boundaries much as in any common hyper-eutectoid carbon steel, though of course the pearlite which would occur in such a steel is not resoluble in this manganese steel.

The *Gamma Theory*, that the martensite stage caused in ways (1) to (4), intermediate between gamma and alpha, is hard and brittle because it is an undercooled solution of gamma in alpha, is based on Tammann's observation * that the undercooling of liquids causes an increase of viscosity. It has been inferred that the curve of this increase, if extrapolated, would result in glass hardness at the room temperature.

This theory meets with two obstacles. First, I do not see that Tammann shows that this increase of viscosity with undercooling is truer of solutions than of pure liquids. If it is not, then why should the undercooled gamma-alpha solution, of which quenched carbon steel is alleged to consist, be glass-brittle when undercooled by $723° † - 23° = 700°$, as in quenched 0·90 per cent. carbon steel, while austenite itself, as we know it in rich manganese and nickel steels, undercooled by say $650° - 23° = 627°$,‡ is so extremely ductile?

Second, Hadfield's quenched manganese steel is a solution of some 19 to 25 per cent. of cementite in gamma iron, undercooled at the room temperature by some 625°. On the gamma theory quenched carbon steel of say 0·40 per cent. of carbon is a like solution in gamma iron undercooled by about 700°, which in addition to 6 per cent. of cementite contains also much alpha iron in solution. On this theory it differs in constitution from Hadfield's steel in that in its solute alpha iron is substituted for some $(19 \text{ to } 25) - 6 = (13 \text{ to } 19)$ per cent. of cementite. Hadfield's is very ductile, the quenched carbon steel is glass-brittle. On this theory, then, to replace in the solute a large quantity of glass-brittle cementite with extremely ductile alpha iron changes the resultant solution from great ductility to glass-brittleness, the solution with the ductile alpha iron being glass-brittle, and that with much glass-brittle cementite being extremely ductile. Is this a theory one would like to administer to one's students?

The *Beta Iron Theory* refers the hardness and brittleness of the state intermediate between gamma and alpha to the presence of an alleged third allotropic modification, comparable and co-ordinate with the known alpha and gamma. In slow cooling this state is passed through or skipped over, and the alpha state reached. In the rapid cooling of carbon steel more or less iron is trapped in this intermediate beta state, though the promptest particles transform as far as the alpha state and the least prompt remain as gamma.

In the slow cooling of rich manganese and nickel steel, unless it is

* Tammann, *Krystallisieren und Schmelzen*, 1903, p. 180.

† The author, "Ae_1, the Equilibrium Temperature for A_1 in Carbon Steel," *Trans. Amer. Inst. Mining Eng.*, to appear, *Bulletin*, June, 1913, p. 1067. I here proposed the symbols Ae_1, Ae_3, etc., to represent the temperature at which the A_1 or the A_3 transformation would occur in the absence of all hysteresis, that is under conditions of true equilibrium, and I inferred from an analysis of the existing data that Ae_1 was about 723°.

23° in this equation given above is taken roughly as the room temperature, that at which the glass-brittleness is commonly observed.

‡ Hadfield and Hopkinson, *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 114. Here manganese evidently lowers the equilibrium temperature, Ae_1, which is about 723° in carbon steel, but at least as low as 650° in Hadfield's manganese steel according to these investigators, who find that the alpha-gamma change begins heating at least as low as 650°. Hysteresis might make Ac_1, which they observed, occur above Ae_1, but nothing can make it occur below Ae_1. Hence Ae_1 is at least as low as 650° in this steel, or about 75° below that of carbon steel, with a fall of some $75 \div 13·4 = 5·6°$ for each per cent. of manganese on an average. This agrees roughly with the inference drawn by the author—"that manganese probably lowers Ae_1 and Ae_3, but by a degree so small as often to be masked by its increasing the lag" ("Discussion of the Existing Data as to the Position of Ae_3," *Bulletin Amer. Inst. Mining Eng.*, June, 1913, p. 1134. *Transactions*, to appear).

extremely slow, very little if any transformation even as far as beta occurs, because of the sluggishness which the nickel or manganese induces. But the transformation can be started by a long enough holding at a temperature, say 550°, which though below Ae_1, and therefore creating a tendency to transform towards alpha, is also high enough to give the mobility needed to enable the transformation to proceed, as before bringing the promptest particles to the alpha state, and the intermediate ones to the beta state, while leaving the least prompt in the gamma state.

In the air hardening of martensitic steels the retarding action of their intermediate proportion of manganese, nickel, or the equivalent, has a like intermediate effect, bringing much iron to the beta state, and some to the alpha state, and leaving some gamma.

The martensitic markings are not those of beta* iron, but represent strains caused by the stresses of the gamma-beta expansion. Because all plastic deformation hardens by decrystallizing, the strains to which the martensitization testifies should contribute to the hardening in all cases in which there is martensitization, as in cases (1) to (4) above.

In the rapid cooling of carbon steel on the beta theory the most prompt particles transform as far as alpha; the least prompt remain gamma; those of intermediate promptness become beta. So with the transformation brought about in ways (2), (3), (4), and (5) above. The beta iron, reinforced by the plastic deformation, explains the hardness and brittleness, the alpha iron the ferro-magnetism; its interlocking with both beta and gamma explains the retentivity; the beta and gamma jointly explain the greater electric resistance.

The gamma-beta transformation explains the marked retardation at about 760° in steels as distinguished from pure iron.

The objections to the beta theory are first that the thermal† curves and those of dilatation‡ and electric conductivity§ of very pure iron, which are just the curves which should disclose the alleged beta state, show in the beta range of temperature no break so marked as would naturally be expected to accompany a transformation of such importance as that from the ductile gamma to the alleged brittle beta; and second, that such break as there is shows far less hysteresis than other transformations in solids do.

* With my assistant, Mr. A. G. Levy, I find that hot etching nearly pure iron with hydrochloric acid in the beta range of temperature causes no martensitic markings, as foreshadowed by Baykoff (*Revue de Metallurgie*, 1909, vol. 6, p. 829, and *Metallurgie*, 1909, vol. 6, p. 743). An objection to Baykoff's evidence is that his steel contained 0·81 per cent. of carbon, and therefore has no range A_2 to A_3 in which beta iron is alleged to exist. It therefore does not show, as Fig. 2 does, that in this alleged beta range the structure is not martensitic but austenitic. Baykoff gives the carbon content of this steel as 0·5–0·8 per cent. C, but this seems to be a misprint for No. 3— 0·81 per cent. C.

In our tests steel of 0·02 per cent. of carbon, kindly given by the American Rolling Mill Company and called by it "ingot iron," was heated in hydrogen to 1,000° for 1½ hours to coarsen its structure, cooled in the hydrogen to 850°, held at 850° for 15 minutes, then etched with hydrochloric acid for 10 seconds, held another hour still at this temperature, 850°, and then cooled in the furnace in a stream of hydrogen. The structure is shown in Fig. 2. No martensitic markings can be found. The shape of the figure marked A in the upper right-hand corner, a sort of five-legged star, is unusual. There is a suggestion here of the persistence of the solidificational dendritic markings, though this specimen was from a billet rolled down from an ingot. There are also suggestions of two independent cellular structures, with austenite grains of great size.

† Burgess and Crowe, *Trans. Amer. Inst. Mining Eng.*, to appear; *Bulletin*, October, 1913, p. 2537.

‡ Benedicks, *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 407.

§ Burgess and Kellberg, *Journ. Washington Academy of Sciences*, 1914, vol. 4, No. 15 (September 19).

Balance of Probabilities.—Each of these three theories has its difficulties.

The gamma theory has difficulty in explaining either the hardness and brittleness of steel hardened in any of the six ways, or the considerable discontinuity at A_2 in the presence of carbon and other impurities.

The beta theory is forced to explain the slightness of the discontinuity in the dilatation and like curves by assuming that, in the absence of carbon and other impurities, the beta-alpha transformation is of a surprising degree of continuity, somewhat after Benedicks's type IV.*

The amorphous theory will have difficulty in explaining hardening No. (6) if this same hardening takes place in the absence of carbon. If it does not, then so far as I see this theory explains all the facts easily except the 760° or A_2 retardation in the presence of carbon. If hardening No. (6) does take place in the absence of carbon, then at present the beta theory would seem to me more credible than the amorphous, and both of them decidedly more credible than the gamma theory.

I acknowledge with great gratitude the very intelligent and zealous work of my assistant, Mr. Arthur G. Levy, B.Sc., F.I.C., in carrying out the experimental work on which the new evidence here offered is based.

Note to Table I.—The material treated was manganese steel kindly given by Knox Taylor, Esq., President of the Taylor-Wharton Iron and Steel Company. It contained about 12·80 per cent. of manganese and 1·24 per cent. of carbon, and was closely like the steel used by Professor Sauveur for his paper "Manganese Steel and the Allotropic Theory," *Bulletin Amer. Inst. Mining Eng.*, September, 1914, p. 2439. It was in the form of cast bars about 12 inches long, 1 inch wide by ½ inch thick. Each hardness determination was made on a separate specimen. The surface was ground away before making the hardness determinations. It was found that the omission of this precaution lessened the apparent hardness. All such results were therefore rejected, though they were often concordant among themselves. The results agree in general with those reached by Hadfield and Hopkinson and by Sauveur, and in addition show that after a long stay at 550° or a short one at 400° the hardness is independent of the rate of cooling.

Specific results of interest are (1) that a bare heating to 600° increased the hardness only slightly, and left the structure austenitic without visible pro-eutectoid cementite, showing the sluggishness of this steel; (2) that after an 800° sojourn slow cooling gave greater hardness than quenching, which may be referred to the opportunity for the formation of beta iron or for the precipitation of pro-eutectoid cementite during the slow cooling. On the other hand a two hours' sojourn at 550° followed by furnace cooling gave less hardness than quenching. This I cannot explain. It may represent the heterogeneousness of the cast material, which was not only extremely dendritic but also contained many cavities. The bar from which the specimens were cut which showed this abnormally small hardness on furnace cooling gave in general less concordant results than the others. The time allowed for preparing this paper for this meeting has not sufficed for investigating this anomaly.

* *Journ. Iron and Steel Inst.*, 1912, No. 2, p. 244.

Dr. T. M. Lowry, F.R.S., and **Mr. R. G. Parker** presented a "Note on Metallic Filings."

They suggested that these were probably cold-worked in an extreme degree. They regarded the remarkable properties of fresh filings of the silver-tin "dental alloy" as due to the presence of a large proportion of Beilby's amorphous phase. The change of density produced by "ageing" these filings at 100° C. is larger than in the case of pure metals, but experiments now in progress have shown that other metallic filings exhibit analogous changes of density when annealed at 100° or even at 80° C. These temperatures are much below those given by Beilby for the annealing temperature of hard-worked alloys, and are very much below the annealing temperatures commonly used in metallurgical work.

THE HARDENING OF STEEL.

The following Paper on "The Hardening of Steel" by **Dr. J. O. Arnold, F.R.S.**, was not received in time for reading at the meeting.

In connection with the hardening of metals, one metal stands out from all others in importance, and that is steel. So far as cutting purposes are concerned, iron containing a carbon range from, say, 0·75 per cent. (cold setts) to 1·5 per cent. (hard turning tools) is involved with reference to plain carbon steel. Hardening is brought about by quenching from a fair red heat, say about 760° C., in cold water. It is common to say that it is unknown why quenched plain carbon steel is hard. This statement, however, involves merely an obvious truism. Equally it is true that it is unknown why the mineral apatite has an abrasive hardness of 5 on Moh's mineral scale, whilst the mineral corundum has a hardness of 9. In the same way, it is not known *why* quenched steel is as hard as quartz, or 7 on Moh's scale, but it is known to those who have carefully studied the matter experimentally *how* steel hardens on quenching. Thus, the question why steel is hard is involved in a mystery common to all hard minerals, and only, therefore, of general academic interest. On the other hand, the manner in which steel hardens is a matter of profound practical importance both to engineers and metallurgists, and the *manner of hardening* is well known to be as follows :—

Taking a saturated steel containing nearly 0·9 per cent. carbon, the whole mass consists of Sorby's compound mineral pearlite, which he, for microscopical reasons, considered to contain about 33 per cent. of a carbide of iron of unknown formula. Further research, however, proved that the correct formula for pearlite is ($21Fe + Fe_3C$), or 87 per cent. of iron, with which is mechanically mixed 13 per cent. of carbide of iron. The mass is, therefore, comparatively soft, because the predominant partner is iron, since the carbide is molecularly associated with only about 12 per cent. of the total iron. On heating pearlite to about 729° C., from a series of centres and over a thermal amplitude of about 3°, the pearlite is transformed to Sorby's amorphous constituent hardenite, which corresponds empirically to the formula $Fe_{24}C$. It, however, probably consists of a solid solution in the iron of the 13 per cent. of Fe_3C present. In such a solution it is obvious that the carbon must be in some molecular association with the whole of the iron. On quenching the solid solution is trapped as such, and when cold has a hardness of quartz. It is clear that this hardness is the inherent property of an amorphous and definite solid solution having a constitutional formula ($21Fe, Fe_3C$). Owing to its thermal instability, hardenite can be "tempered," i.e. any desired amount of the dissolved Fe_3C can be precipitated from solution in the iron, and any desired modification in the hardness of the quenched steel be so

produced. At a straw temper, say 235° C., only a small part of the hardenite reverts to troostitic pearlite ; at a blue temper, say 295° C., a much larger quantity of pearlite is produced, with the corresponding reduction in the abrasion hardness of the mass. If tempered too far, so as to make troostitic pearlite the preponderating constituent, the steel becomes too soft for cutting purposes. At 400° C. a blue-black temper, the hardenite reverts altogether to pearlite, and the mass has become relatively soft again.

In this saturated steel there is only a single absorption point, having its maximum at about 729° C., and this absorption point has the formula $Ac_{(123)}$. In unsaturated steel, however, containing 0·2 per cent. carbon there are three absorption points, Ac_1 at 729° C. ; Ac_2, which has an amplitude of about 20°, namely from 745° to 765° C.; and Ac_3, the maximum of which occurs at about 830° C. Thus there are three ranges of temperature divided by these critical absorption points. The range from atmospheric temperature to Ac_2 may be conveniently called the Alpha range ; between Ac_2 and Ac_3 constitutes the Beta range ; above Ac_3 is the Gamma range.* On reaching Ac_1 the whole of the carbide of iron may readily be shown, on rapid quenching, to have totally dissolved in the Alpha range at a temperature of about 730° C. Many metallurgists think that the point Ac_1 is really a combined point, Ac_{123}. There is no proof of this, nor any reason to think it is so. If this were true, on cooling unsaturated steels, as the carbon increased the points Ar_3 and Ar_2 would not only descend, but would become smaller and smaller. Carefully obtained experimental data have shown that there is no evidence of this. Also, it is certain that in annealed steels the Fe_3C is embedded in well marked striæ in iron undoubtedly associated with the Alpha range, and that this iron and the carbide striæ interpenetrate over an amplitude of about 3° C. to form a solid solution of clear-cut yellow and micrographically amorphous hardenite, which replaces the two-ninths of pearlite originally present in the 0·2 per cent. carbon steel now under discussion. This hardenite, on further heating, diffuses into the free iron as the temperature rises and homogeneity is obtained about 950° C. The points Ac_2 and Ac_3 have no effect upon the rate of this diffusion, nor has time any noticeable influence. The diffusion is determined alone by the rising temperature, and at any given temperature, one minute at that temperature will produce a diffusion indistinguishable micrographically from the diffusion produced by keeping the steel 60 minutes at the same temperature. The hardening of low carbon (0·65 per cent.) high tungsten (20 per cent.) high-speed steel depends on the transformation of tungsten pearlite to tungsten hardenite,

* In view of a misinterpretation of the writer's meaning in using the expressions alpha, beta, and gamma ranges of temperature (see *Journal of the Iron and Steel Institute*, No. 1, 1914, 3rd para., p. 203), he here quotes a paragraph from the *Journal of the Iron and Steel Institute*, No. 2, 1905, p. 64, embodying remarks made by him at the Sheffield Meeting of the Institute.

"He wished to reiterate the point so ably put forward by Mr. McWilliam, that during the whole of the paper they specifically stated that they were referring, not to alpha, beta, and gamma varieties of iron, but to ranges of temperature which they carefully specified, and he did not think there was any ground for Mr. Stead's suggestion that they were coming round to the view that these were allotropic modifications of iron, because they did not know whether this was so or not. The ranges of temperature they did know, and they were distinctly specified."

since about 12 per cent. of tungsten completely expels carbide of iron from the mass. Tungsten hardenite forms progressively from about 850° C. to 1,200° C.; hence, to ensure the complete transformation of tungsten pearlite to tungsten hardenite it is customary to heat such steel to, say, 1,250° C., and then quench out in oil or in a blast of compressed air. Vanadium expels carbide of iron when only about 5 per cent. of the element is present, forming a vanadium pearlite, which transforms to vanadium hardenite somewhat abruptly at about 1,400° C. Vanadium hardenite is as hard as topaz, or 8 on Moh's scale. Thus very high vanadium steel containing, say, 1 per cent. carbon, when quenched from red or yellow temperatures, remains quite soft, and must be hardened from a white heat to ensure the formation of vanadium hardenite. Tungsten and vanadium hardenites, unlike iron hardenite, are stable at a moderate red heat. It may be noted that in steels containing, say, 10 per cent. vanadium and 1 per cent. carbon the double point Ar_2 occurs at about 850° C.; hence, on heating, Ac_1 is about 550° C. above Ac_2, and only when the carbon change at Ac_1 takes place does the steel become hard. These effects seem to preclude any substantial influence of allotropy, amorphous cements, internal stresses, and twinning of crystals in the production of hardness; indeed, it is known that in other metals there is no difference in the hardness between ordinary and twinned crystals. Indeed, theoretically, twinning would rather seem to favour a diminution than an increase of hardness. It may also be noted that these theories, when considered as a whole, tend mutually to contradict each other. No modern theories have disturbed to any great extent the explanation of the hardening of steel made by Henry Clifton Sorby a lifetime ago.

DISCUSSION.

Sir Robert Hadfield opened the general discussion which followed the reading of the Papers.

I much regret that Professor Cohen is unable to be present to-night. We all greatly admire his country—Holland—and feel special sympathy with her at the present time owing to the difficult position in which she is placed during the present lamentable war.

The Society is to be congratulated on receiving a Paper all the way from America from the eminent Professor Howe, also on the presence of Professor Turner of Birmingham, who was one of the first of those who started systematic observations on the hardness of metals.

I am glad to see that Professor Howe seems to be coming back to the carbonist theory, and that Dr. Stead emphasizes the fact that the main factor in the cause of the hardness of iron alloys is carbon.

I still think that the question we should study is that relating to the combinations which take place between iron and carbon and from which we obtain intense hardness when heated carbon steel is quenched. I feel so strongly on this matter that I have offered through the Iron and Steel Institute a prize of £200 for the best study of carbides of iron and iron alloys generally. I hope Members of this Society will take part in the competition, full particulars of which can be obtained from the Secretary of the Iron and Steel Institute, 28 Victoria Street, Westminster, London, S.W.

Dr. J. E. Stead, F.R.S. (*communicated*) : It is my opinion that we have not sufficient data on which to found any definite conclusion as to why steel is hardened by heating to above Ac_{1-2-3} followed by quenching. One thing is certain, and that is the carbon is mainly responsible. The different behaviour of hardened and annealed steel when treated with chemical reagents, such as sulphuric and nitric acid, is absolute proof that there is a difference in the chemical constitution of the two. The difficulty is, and always will be, to determine what that difference really is. The inducement the President has offered to study this side of the question is likely to lead to valuable results.

It is certain that the discussion of the question of hardening of steel and other metals must lead to the elimination of untenable hypotheses and to a clearing of the way for the truth.

The allotropic theory of Osmond was never advanced as other than one of a tentative character, and I have always regarded it as such.

The purely solid solution hypothesis, that the hardness of quenched metals is due to intimate solid mixture, may be one of several which point in the right direction.

The internal stress hypothesis may be more or less correct, but it is well to remember that no matter how much 0·90 per cent. carbon steel is stressed and distorted in the cold, it never can be made intensely hard or become what is described as glass hard.

I have for many years studied the iron and phosphorus compounds. Iron saturated with about 1·7 per cent. phosphorus is difficult to drill, yet Cleveland pig iron or any grey iron containing even 2 per cent. or more phosphorus can be readily machined. The difference is coincident with a difference in the "phosphorus condition."

In the hard material the phosphorus is in solid solution, Fe_3P in iron, while in the pig irons the Fe_3P is in a free and separate state. In one of the Mexican meteorites the greater part of the phosphorus, 0·27 per cent., exists

in independent crystals of $(FeNi)_3P$, and the metal is very soft. On heating to near the melting-point the free phosphides diffuse and pass into solid solution, and the metal when cold is sensibly harder. Further, when treated with acid practically no phosphine gas is evolved from the metal containing free phosphide, but much of that gas is evolved on similarly treating the other metal containing the phosphide in solid solution.

There is a close analogy between steel, and iron containing phosphorus, but it is premature to state that solid solution alone is responsible for the hardness of quenched steel.

The meteorite above referred to contained at least 100 twin laminæ of the Neumann type in each eighth of an inch (produced no doubt by strain during very slow cooling of the original large mass). These laminæ, which I have proved beyond all doubt to be twins, are eliminated on heating to 800° C., but the metal did not become sensibly softer. Twinning, therefore, is no indication of hardness. The same steel containing 0·90 per cent. carbon, whether quenched from 750° C. or 900° C., is equally hard. The first has a barely detectable martensite structure, while in the second that structure is very pronounced. The internal stresses presumably must be greater in the second than in the first, yet the hardness is not different.

Nickel steel containing 4 per cent. nickel and 0·4 per cent. carbon on quenching from 900° C. is hard and brittle, and has a pronounced and gross martensite structure, yet after re-heating to 500° C. for a short time the structure remains; indeed, one structure may be taken for the other, but the quenched metal is hard and the annealed metal soft. Difference in this case is certainly in the carbon condition.

In conclusion, I must again state that we have not sufficient data on which to base dogmatic conclusions. All hypotheses, the results of careful observation, may be tentatively held till they are proved untenable or otherwise. It is most desirable that more attention should be given to the study of carbon condition, for there can be little doubt that on this mainly depends the extreme hardness of steel.

Mr. Andrew McCance (*communicated*): I do not wish to question in any way the immense service that Dr. Beilby's theory of the amorphous phase has done to the study of the hardening of metals by deformation, and the insight and knowledge it has given us of the crystalline structure. But as new facts appear it is necessary to inquire if these are explained with the same elegance and facility as the older facts were. I would emphasize particularly the hardness produced without permanent deformation by the action of high pressures on metals, and the difficulties of explaining the magnetic properties of strained alpha and strained gamma iron. Has it been shown experimentally that the amorphous state is *actually* harder than the crystalline state for any substance at the same temperature; is transparent glass, for instance, at ordinary temperatures harder than the same glass devitrified? Also, since the temperature-hardness curve for the crystalline state is different from that of the amorphous state, and at higher temperatures the amorphous state is the softer, it follows that there will be a temperature at which permanent deformation softens instead of hardening.

Regarding the magnetic properties, it is admitted, of course, that our knowledge of magnetism is still highly speculative, but the electron theory of Langevin-Weiss gives values of fundamental physical constants which are in complete agreement with other independent calculations, proving that the primary assumptions are true.

Mr. Humfrey's views are almost identical with those which I have published, and he also realizes the difficulty regarding the corelation of the

magnetic properties with the amorphous phase theory. He gets over this, however, by assuming that in the crystalline space lattice it is the molecules which are regularly spaced, and that in each molecule the atoms are similarly arranged. This is in contradiction with the stated views of physicists that in a crystalline space lattice it is the atoms which are alone concerned, and that in a binary compound the space lattices of the two elements are mutually interplaced, giving rise to a new space lattice formed by the atoms of both.

His view that structureless martensite is formed when all the austenite has been transformed to amorphous alpha iron, while the more prominent structure obtained from a higher quenching temperature is due to the retention of much austenite, is not in accordance with experimental evidence, for I have shown that a steel containing 0·86 per cent. carbon has the same percentage of gamma iron whether it is quenched from 760° or 1,000° C. The martensitic structure represents the cleavage planes of the gamma iron crystals at the temperature of quenching, and the apparent lack of structure of steels quenched from 760° C. is due to the very small size of these crystals.

In general, however, my own views and his are in complete agreement.

Professor T. Turner (University of Birmingham) said they as visitors were much indebted to the Faraday Society for providing an opportunity of discussing a subject of so great importance in the arts and manufactures. Sometimes a metal is required to be soft, and sometimes its value depends on its being hard, and it is important to know the reason why a particular sample is hard or not hard. Dr. Beilby's remarks in reference to the importance of further knowledge of the molecular structure of the metals and the variation of specific heat were very suggestive. It has long been noticed that the hardness of pure metals is proportional to their density divided by their atomic weight.* It therefore varies inversely as the atomic volume, and is greater the more closely the atoms, or rather the molecules, are packed together in the material.†

Passing from pure metals, there would appear to be two distinct kinds of increased hardness, each of which depends on an alteration in molecular distances. The mental conception that the difference in hardness ultimately depends on the alteration in the molecular structure of the material appears to be justified. Mechanical deformation increases the hardness, and chemical alteration, which changes the packing and nearness of the molecules, also produces additional hardness. These two kinds of added hardness should be kept mentally distinct.

Metals are practically incompressible and are impermeable by gases. Hence the molecular interspaces are probably very small, and this is in accord with the fact that the change of volume due to the result of work upon a metal is relatively very small, although the hardness may be enormously increased. Therefore, as the change in the molecular distance caused by work, or by solution of one metal in another, is very small, the actual molecular distances themselves must also be very small.

It has been pointed out by Dr. Brislee that metals may become lighter by rolling. As a matter of fact the first effect is generally that of increasing the density as a result of squeezing and consequent closing of the pores. With further work the density is diminished. The effect of rolling a metal is usually supposed to be that of compression, but examination will show that the material just before it leaves the rolls is in tension, while as it enters the rolls it is in compression.

* Bottone, *Chem. News*, 1873, p. 215.
† T. Turner, *Chem. News*, 1887, vol. lv., p. 179.

The next point to consider is the effect produced by solution on molecular distance and therefore on hardness. Dr. Lowry mentioned, in reading Dr. Desch's paper, that in solid solutions we always have an increase in hardness. I believe he also said that the intermetallic compounds are softer than the metals of which they are composed. The latter rule is by no means invariable, as has been shown in work on the copper-zinc series of alloys, in which the compound, Cu_2Zn_3, is very much harder than either of its constituents.* In the copper-tin series also a hard compound is well known.

When one substance dissolves in another, very large forces must be brought into play, as there must be a very considerable attraction between the particles of the solvent and the particles of the solute. Now those forces must bring the molecules closer together, as Tammann points out, and therefore we can have a similar effect produced by chemical means to that produced by mechanical means in the first kind of hardness. One important difference between the two means of producing hardness is that as far as mechanical means are concerned it is seldom possible to more than double the tenacity of the metal, but with solid solutions it is frequently possible to obtain a very considerable increase of tenacity accompanying the increase of hardness.

He (the speaker) preferred to explain almost the whole of the changes which take place in various steels by the suggestion that the carbides are taken in or out of solution at different temperatures, and as the solid solutions vary in character and concentration, different degrees of hardness result. The solubility of the carbides would doubtless depend, at least in part, on any allotropic changes in the iron. Internal strain may also produce considerable effect.

Although the presence of twinned crystals indicates there has been a previous strain, it does not prove that the metal is hard. The material may have been hard at one stage of its existence, but the presence of twinned crystals does not prove the metal to be still hard. The suggestion is rather the other way, namely, that annealing has ensued. Thus hard rolled brass does not show twinned crystals, but when it has been annealed twinning is plainly seen. This indicates that the metal has been in the hardened state once, and now it has an opportunity of showing the result of what then occurred.

Dr. Lowry referred to annealing at a specially low temperature The speaker used to show an experiment to his students with a fusible alloy containing 8 parts of bismuth, 3 of tin, and 5 of lead, which is brittle when cast quickly in water, but which is annealed if held in the hand. At the same time very appreciable heat is evolved.

Dr. W. H. Hatfield (Sheffield): I have been extremely interested in the whole of the Papers given this evening, and I am sure that the Society will have done much to advance the theoretical side of the subject by this discussion. It seems to me that at least three of the theories brought forward to-night are the direct results of Dr. Beilby's work and his subsequent writings on the amorphous theory of the hardening of metals. Dr. Beilby's work has undoubtedly led to a considerable advance in our understanding of this subject of hardness, and, whether or not the amorphous theory will finally prove tenable, his contributions have led to such a wide discussion of the subject that they have undoubtedly been responsible for considerable advances in our knowledge. Some time ago I had the pleasure of receiving from Dr. Beilby a complete set of his works in this field, and there is no doubt it ought to receive the attention of any one interested in the problem before

* *Journ. Institute of Metals*, 1909, vol. ii., p. 130.

us. As an iron and steel metallurgist I naturally endeavoured to see how and where his theory would fit in with the facts which I meet in my daily practice. What do I find? As regards the effect of cold work on pure metals, his amorphous theory would appear to apply, but as regards the question of the hardening of steel, I am doubtful. The quenched hardness of carbon steel is one of the outstanding important phenomena in physical metallurgy, and to my mind appears quite unique. For instance, if you take a piece of pure iron and submit it to cold work, you increase in considerable measure both the tenacity and hardness. Take the same piece of pure iron and quench it from the gamma range and the hardness produced is inconsiderable. Now, if carbon be added to this pure iron and the quenching is done from the gamma range, you produce with the greatest ease a hardness that is out of all proportion to the hardness obtained by cold work or by quenching of other industrial metals and metallic compounds. I should like to recall to the meeting the interesting experiments executed by Dr. Arnold a number of years ago. As he had not at his disposal pure iron, he experimented with iron containing 0·07 per cent. of carbon, and this material he quenched at different temperatures up to well within the gamma range of temperatures. This material, quenched from 780° C., had a tensile strength of 29 tons per square inch, and when quenched from well within the gamma range its tensile strength was still only 32 tons. Obviously then, after putting upon the iron all the "work" and internal stress which quenching from such high temperature must do, hardness and hence the hard amorphous phase is not obtained. But, put the necessary quantity of carbon into the composition and the quenched hardness of steel is obtained out of all proportion to any hardness to be obtained by cold working. In my opinion this central point must always be kept before us when considering the subject. I have already said I was interested and indeed fascinated by the logic of the amorphous theory as originally advanced by Dr. Beilby and subsequently developed in different directions by Dr. Rosenhain and Mr. Humfrey, and in endeavouring to explain hardness by quenching in its terms I arrived logically and quite independently at the identical point of view expressed by Mr. Humfrey in his Paper of this evening. It is obvious that when the gamma iron changes to alpha iron (beta iron being considered non-existent) the metal passes through the mobile or amorphous phase. Now *if* the amorphous phase is intensely hard and *if* in quenching you can trap it *en masse*, you would appear to have a logical explanation of the quenched hardness according to the amorphous theory. But, it may be pointed out, there are a number of considerations which require carefully weighing before such a view can be accepted. For instance, Mr. Humfrey suggests that troostite, the first decomposition product from the solid solution, is amorphous iron intermixed with cementite. Now, if this troostite is amorphous iron, it should be equally hard with the martensite from which it is derived. That is not the case, troostite being distinctly softer. Furthermore, if the troostite is amorphous iron, is it not fair to presume that the cementite is in solution? At any rate this is the view generally held as to the solubility of the cementite in amorphous iron. The original idea still held by a number of the exponents of the amorphous theory is that the amorphous phase produced in the transference from gamma to alpha iron is identical with the undercooled liquid phase, and this being so, the cementite would be soluble. As a matter of fact, the amorphous phase that might be considered to be produced during the change from gamma to alpha must be an entirely distinct phase from that of the undercooled liquid, and Humfrey is assuming this position when he says that the secondary amorphous phase does not dissolve carbon or carbide; hence his suggestion that troostite

does not contain the carbon in solution. After careful consideration, however, I have come to the conclusion that the amorphous theory does not offer a completely satisfactory explanation either when considered from Dr. Edward's and Dr. Carpenter's or from Mr. Humfrey's standpoint.

Turning to Mr. McCance's Paper, I should like to draw his attention to his preliminary statement as to the three methods of producing hardness in a pure metal. His second method, i.e. that of adding other metals, etc., cannot be considered, since the hardness which may, or may not, result is not the hardness of the *pure* metal but of the *alloy* produced. In summing up the question of the hardening of steel in my own mind, I feel distinctly driven back upon the original idea, well supported as it is by Dr. Desch's Paper before us this evening, that hardness of quenched steel is due to the inherent hardness of the solid solution of carbide in iron trapped by quenching. This quenched solid solution of such outstanding properties is hard like a number of other hard substances, and will probably have to be treated from an entirely different standpoint to that before us in the amorphous idea. It must be borne in mind that whilst Dr. Beilby has established the existence of the mobile or amorphous phase under certain conditions, the explanations offered by the amorphous theory of the hardening of steel, and indeed the hardening of cold-worked metals, are, as yet, only theories, and it is well that we should bear in mind that the so-called amorphous phase, whether in cold-worked metals or in quenched metals, is "ultramicroscopic."

In conclusion, might I ask Dr. Beilby, whose brilliant work we all so much admire, to recapitulate from his point of view the definite facts upon which the amorphous idea stands as distinct from the bulk of hypothetical matter that has accumulated round it owing to the efforts of some of his strenuous and enthusiastic disciples?

Mr. T. G. Elliot: Speaking as a chemist it is perhaps not unnatural that, I think, since the physicists have taken hold of the subject it has not been simplified in any way. Indeed, a perusal of the papers presented for discussion shows how involved it has become. This is particularly the case with regard to the hardening of iron, which years ago was thought to be dependent on the addition of carbon.

After an interval during which the hard beta iron theory has been strongly supported, it is interesting to see that Dr. Rosenhain, in his new book on *Physical Metallurgy*, gives a certain amount of support to a combined, carbon and amorphous cement theory; in other words, carbon may have something to do with the hardening of steel after all!

Professor Howe's Paper has particularly interested me, dealing as it does so much with Hadfield's manganese steel. In Sir Robert Hadfield's laboratory we have long noted the blackening effect of sodium picrate on the martensitic like needles mentioned in the footnote on page 267. In other words, there we have a martensitic structure which, according to Professor Howe, is not martensite. But what is martensite? Osmond described a *tempered steel* exhibiting a martensitic structure as a pseudomorph; it had the structure of martensite with the properties of troostite. At any rate, it is apparent that there is a very close connection between the martensitic structure, the falling out of solid solution of carbide, and the hardness of steel. Whilst there are undoubtedly other contributing causes of this hardness—such as the effect of stress—in my opinion the study of the relationship between iron, carbon, and manganese opens the most promising field for research on the subject.

Dr. F. J. Brislee (Roby): I have come rather to learn than to teach. I would like to ask Dr. Beilby one or two questions. When a metal changes

from the crystalline to the amorphous state by mechanical work, as is often the case, should the tensile strength necessarily increase? I found that the density of aluminium decreased with working and increased with annealing. When worked, all the desirable properties disappeared. High tensile strength was aimed at, and the resulting metal may have had a strength of 16 tons per square inch, but it could not be bent at right angles without breaking.

I should like to know from Dr. Beilby if the passage from the amorphous to the crystalline state would have a definite transition-point, and if so, whether transition from the amorphous to the crystalline state, which in the case of aluminium increases its density, is identical with the annealing-point. I found that a sharp change took place in overworked aluminium at 230° C. Further, it might be pointed out that when a metal assumes an amorphous state, this is not necessarily an allotropic form of the metal.

Professor Cohen's contribution on the disintegration of lead is very interesting, as this may explain the cause of the trouble in underground lead, especially lead-covered electrical cables.

Mr. S. A. Main (Sheffield): In considering the various theories put forward it will be noticed how really little work has been done towards correlating in a quantitative manner the degree of hardness and the cause assigned for it. In fact, hardness is to a large extent regarded merely as a quality in contradistinction to softness. Hardness is of course a measurable quantity and there are degrees of hardness. It must be admitted that such quantitative confirmation is in many cases difficult to obtain. The difficulty is not lessened by the unsatisfactory nature of our present means of measuring hardness, especially with regard to degrees of hardness exceeding what is known as "glass-scratching hardness," in which is comprised the hardness of quenched steel, which it will be agreed is one of the chief problems in connection with the hardness of metals. It is to be hoped that the efforts of the Committee of the Institution of Mechanical Engineers may lead to hardness testing being placed on a more satisfactory basis. Whatever the cause, however, this lack of quantitative connection is an indication of the weakness of our present knowledge of the cause of hardness in metals.

For this reason the theory of the hardness of solid solutions dealt with in the Paper by Dr. Desch has one advantage over many other theories, in that the connection between hardness and its assigned cause—the attractions of the molecules—is carried to the extent of a quantitative relation which is even expressed by a physical equation. Moreover, it is much easier to associate hardness, a mechanical quality, in one's mind with the forces of attraction or cohesion between the molecules, than with the more or less hypothetical attributes of a more or less hypothetical constituent.

The simple faith of some allotropists in a hard form of iron is not much disturbed by the failure of beta iron. With characteristic resource they turn to yet another, but more obscure, form of iron; more obscure, that is, because we could always get a tangible specimen of unadulterated beta by heating pure iron to, say, 800°, while apparently we cannot handle a specimen of amorphous iron by itself and without the awkward interference of carbon.

Unfortunately for amorphous iron, it is just as vulnerable as beta at vital points. The grounds on which its intrinsic hardness is based are left very much to the imagination; the fact that some of the hardest materials known, e.g. diamond, quartz, carborundum, corundum, are essentially non-amorphous does not help us, nor does the method of reasoning afforded by the allotropists for the hardness of beta iron; the latter at about 780° C. having been

demonstrated by tenacity tests to be a little harder than alpha, we were asked to imagine that therefore at ordinary temperatures beta was many times harder than alpha; at this same temperature, 780° C., alpha iron is, we are told, rapidly softening with a view to becoming liquid alpha or amorphous iron (being prevented only by the timely intervention of A_2); that is, amorphous iron or liquid alpha softer than solid alpha, as we might expect. Is not amorphous iron therefore many times *softer* than alpha at ordinary temperature? On the contrary, we are to understand it is many times harder.

Again, from the point of view of magnetic qualities, quenched carbon steels, though hard, have a saturation specific magnetism of as much as 90 per cent. that of pure iron. We are not told what the magnetic properties of amorphous iron are, but as liquid alpha it is presumably, like other liquids and like liquid iron as we know it, practically non-magnetic. There is not much room for a non-magnetic constituent in a material of 90 per cent. magnetism—no more, in fact, than there was for beta.

How does this theory account for the hardness in the case of a 0·6 per cent. carbon steel, heated and allowed to cool through the Ar_{32} point as slowly as possible, giving every opportunity for the complicated processes described, from gamma into amorphous and amorphous into alpha, to take place, including most of the residual gamma iron supposed to be in solution below Ar_{32}, but quenching from just above Ar_1; hardness, that is to say, with little or no amorphous iron?

Surely when the hardness of solid solutions is such an acknowledged fact, and indeed is confirmed by physico-mathematical investigation in some simple cases, it is not claiming too much to say that the hardness of quenched carbon steel is the hardness of a solution of carbon, an element which is itself capable of the highest degree of hardness, in iron—whether as carbide or not. At least, this aspect of the question appears to offer more substantial grounds for investigation than the hypothesis of inherent hardness in the iron.

Sir T. Kirke Rose: With regard to the twinning produced in tin by bending, I should like to ask Professor Edwards and Professor Carpenter how long they left the tin before examination, because tin anneals itself at the ordinary temperature in 24 hours. It follows that unless the photomicrographs were taken immediately after bending, the twinning shown in them might be due not to straining but to subsequent annealing.

(*Written communication*): As the temperature of annealing of tin does not appear to be generally known, I may point out that the results of my observations on the subject are given in the 43rd Annual Report of the Mint, 1912, p. 54. They are to the effect that the lowest temperature at which the softening of hard-rolled tin begins to be perceptible is about 10° C., and that the softening is practically complete in 24 hours at 15° and in less than a minute at 100°.

A summary of the observations themselves, which have not been published previously, is as follows:—

The mean hardness numbers given below are measurements by the Shore scleroscope, with the magnifier hammer. On this scale soft lead is 2, soft gold 5·5, and hard-rolled gold 33 to 35.

	Hardness Number.
Tin, cast	4·0 to 4·2
Tin rolled at — 25° C. (ratio of thickness, 8 to 1) ...	13
The same after 30 min. at — 20°	14
„ „ „ „ 0°	13
„ „ 1½ hours at 14°	10 to 10·5

	Hardness Number.
The same after 20 hours at 13°	6·3 to 6·6
„ „ 24 „ „ 15°	4·5
Tin rolled at 15°	9·5 to 10
The same after 97 days at the ordinary temperature	4·5
„ „ 217 days	4·2
Heated to 50° and quenched	8·6
„ 100° „ „	5·2

A different sample was used for each of the above experiments.

A strip of tin is "springy" just after being rolled, but by the next day the springiness has disappeared. As in other metals,* so in tin, there does not appear to be any critical *point* in the temperature of annealing, but there is a *critical range* of temperature within which the rate of annealing undergoes a rapid change. In the case of pure metals, the critical range of annealing is short, usually about 20°, but in impure metals and alloys the range is much longer, often amounting to 200° or 300°. Annealing here denotes simultaneous softening and recrystallization, but the new crystals proceed to grow for some time if the temperature is maintained or increased, without any further marked diminution of hardness. These facts do not rest on any theoretical considerations.

Dr. Lowry's observation as to the temperature of annealing of his dental alloy, $AgSn_3$, falls into line with those of other alloys, whose temperatures of annealing are often above that of the predominant metal present. †

Dr. G. T. Beilby (*partly communicated*) : In connection with experimental work in the field covered by Section I, I have made a number of observations on the behaviour of pure iron. These observations show that in most respects iron falls in line with the other pure ductile metals, but the allotropy indicated by its thermal behaviour necessarily complicates the observations of electrical conductivity and thermoelectric potential. The magnetic properties may be expected to supply valuable information on the molecular arrangement in the two states, but I venture to suggest that these ought to be worked out exhaustively on the purest iron obtainable. Among the impurities to be shunned, hydrogen and nitrogen must not be ignored. My experiments show that while it is possible by cold working to raise the hardness or rigidity of pure iron to a very high point, it never reaches the hardness of tool steel. As regards the part played by carbon in the hardening of steel, I have not the expert knowledge of the subject which would entitle me to express strong views on the various theories which have been advanced, but from the point of view of a worker in the field of Section I it would appear to me perfectly natural that the presence of the small, strongly-cohesive molecules of carbon in an aggregate consisting mainly of iron molecules might add not only to the "intrinsic cohesive force" of the aggregate but also to its "effective cohesive force." This is only another way of putting an idea which we really owe to Roberts-Austen.

I do not like the term "amorphous" any more than Mr. McCance does. I often regret not having adhered to "vitreous," which is the term I applied to the flowed surface layer on metals in 1901. "Amorphous" is too purely negative, while "vitreous" is specific and at the same time non-committal. But I gather from Mr. McCance's communication that he objects not merely to the name but also to the explanation of the hard and soft states with which

* *Nature*, November 21, 1912, p. 330.
† See *Jour. Inst. of Metals*, vol. viii. (1912), p. 113.

it is associated. In the argument which has been developed in the Paper which will be printed with this discussion I have tried to make a clear distinction between the facts and the inferences from these facts on which the amorphous theory is founded. From this it will be obvious that the keystone of the theory is *the instantaneous liquefaction and solidification of sheets of molecules during mechanical deformation*. This assumption is based on a very strong body of circumstantial evidence, and if it is true in the cases which constitute this body of evidence, I think it must be admitted that it is a truth of general application. There is evidence that in particular cases small displacements of orientation in lamellæ or grains may be restored to their original state without any disturbance of the original crystalline arrangement. If our observations had to be limited to cases of this description, it is to be feared that our knowledge of the subject would be very much more imperfect than it is to-day. But the more obvious and well-marked cases are fortunately at our disposal, and it is a strength rather than a weakness in our position that we should develop these fully before dealing with the less pronounced cases.

Mr. McCance believes that the magnetic phenomena in the two states tell against the existence of a really non-crystalline state. This matter has already been referred to in the Paper above. He also cites the supposed cases of hardening by a hydrostatic pressure of 10,000 kgs. per cm². I have not seen Hanriot's paper, but shall make a point of doing so. In the absence of details of experimental methods and data, it would be unfair to criticize his results, but as these are presented in Mr. McCance's Paper they do not satisfy me that they prove that permanent deformation can result from uniform compression in all directions. It is quite conceivable that internal movements due to differential pressures within M. Hanriot's cubes might occur even under externally applied hydrostatic pressure. The paper by Messrs. Johnston and Adams in the *Journal* of the American Chemical Society in May 1912 contains much interesting information on changes of density in solids under high pressures.

Sir Robert Hadfield, who had continually interpolated valuable and illuminating comments during the discussion, in his reply drew special attention to the Paper by Professor Howe.

The more one investigates, said Sir Robert, the more it is apparent that there is some extraordinary change in the combination of the carbon with iron, and it was for this reason that he had offered his prize for a research. This had been offered both in this country and in America because, in his opinion, we in this country on the scientific side, and the Americans on the practical side, had done more than any other countries in the world to elucidate the difficulties surrounding the problem. Between us we ought to find some means of more clearly understanding what it is that takes place in the hardening of carbon steel. With all due deference to the Papers placed before the meeting, he continued, he could not say there was one that threw light on what really happened when a piece of carbon steel was changed from a soft to a hard condition. All these investigators were doing good work, but they did not seem to bring us any nearer the solution of what was taking place. The point to be studied was to try and find out what is the combination that takes place between the iron and the carbon which brings about the intense hardness when a piece of carbon steel is quenched, and it was in this connection that he regarded as of special importance the "balance of probabilities" in Professor Howe's Paper.

Dr. J. E. Stead had expressed the opinion that we have not sufficient data upon which to found any definite conclusion as to the process known as the hardening of steel by quenching. It was most desirable, therefore, that more

attention should be given to the study of the carbon condition, for there could be but little doubt that on it depends mainly the extreme hardness of steel.

With this view Sir Robert Hadfield fully agreed. There was, he said, one thing certain, viz., that carbon was mainly responsible. Some investigators seemed to get away from this important fact, but there was undoubtedly a difference in the chemical constitution, and the difficulty was to determine that difference. Osmond's theory he regarded as only tentative, and the theory of internal stress, an attempt to explain the hardening of steel in a new direction, put forward in Mr. McCance's Paper, might be the correct one; but it was well to remember that, no matter how much carbon steel might be stressed or disturbed in the cold, it could never be made glass hard. We had not, he concluded, sufficient data upon which to base dogmatic conclusions and hypotheses, and results of careful observations must hold until they had been proved untenable.

Referring to Mr. Heathcote's demonstration of instruments for the determination of hardness, Sir Robert Hadfield, as an instance of the lack of information on these matters, said that a short time ago he wished to obtain some particulars of the hardness of quartz and diamond compared with the hardness of steel, but he could not find the slightest information. This only served to show how ignorant we all were. He made some tests of his own, and found by the Shore scleroscope a rebound test of not less than 120, whereas the highest hardness obtained with steel up to the present was between 80 and 90. The 120 was equal to about 700 Brinell hardness number. The current idea conveyed in some of the Papers seemed to be that a hardened metal was in a state of strain, but he could not agree with that for a practical reason. A projectile would go through a plate of calibre thickness unbroken. It was impossible to conceive this happening if the metal was in a strained condition. This related to capped shot, but the cap was dispersed so quickly that the point of the shot had still to take an enormous crushing stress, and it was in an exceedingly hard condition, probably over 700 Brinell hardness number. If the point was in a strained condition, surely the projectile would go to pieces, but it did not do so.

Dr. C. A. Edwards wrote that he wished briefly to refer to a few points that had been raised in the general discussion.

Dr. Stead cited two instances which he considered were incompatible with the theory advanced by Professor Carpenter and the writer. The first was the case of the meteorite which contained Neumann lines or twin crystals, but which did not become "sensibly softer" when these twin crystals were removed by annealing at 800° C. In the absence of more complete data it is not an easy matter to discuss this question, but it would seem from Dr. Stead's remarks that this treatment does bring about a certain amount of softening. Heating to 800° C. to remove the Neumann lines may also cause some of the free phosphorus to go into solution, and this would harden the mass, and thus work in the opposite direction to the softening brought about by removing the twin crystals.

In connection with the above and other criticisms of a similar nature, it seems necessary to reiterate that Professor Carpenter and the writer do not regard the great hardness which is produced by quenching steels as being entirely caused by crystal twinning. The chemical composition is admitted to play a most important rôle in this respect.

The second case mentioned by Dr. Stead was the hardened nickel steel which becomes soft, although the martensitic markings remain, after annealing at 500° C. The writer's explanation of this is, that at 500° C. the greater part

of the amorphous material becomes recrystallized, but the structure as seen under the microscope is not thereby materially influenced. This is very similar to what Goerens finds in the case of cold-worked steels, who states that the effect of cold working disappears at 520° C.

The fact that a 0·9 per cent. carbon steel possesses approximately the same degree of hardness when quenched from 750° and 900° C. is exactly what would be expected from the theory of hardening which is based upon the chemical composition and crystal twinning. According to this theory the degree of twinning is proportional to the amount of the carbide change which is suppressed by quenching. Hence it is practically independent of the quenching temperature: the twinning will be approximately the same whether the steel is quenched from 750° or 900° C.

The more obvious acicular markings which are evident after quenching from high temperatures do not indicate a greater degree of twinning.

Dr. W. Rosenhain, F.R.S., in a communication dated February 15, 1915, wrote that absence from England had unfortunately prevented him from taking the part which he would have wished in the discussion on the hardening of metals. In the present written contribution to the discussion, made at the eleventh hour at the request of the President and Secretary, he felt that it would be difficult to deal adequately with the numerous questions which had been raised.

It was interesting to notice that three of those who contributed papers, viz. Dr. Beilby, Mr. Humfrey, and Professor Edwards, were agreed that the hardness of quenched steel, and indeed of all metals and alloys hardened by quenching or by cold working, was due to the presence of metal in the amorphous condition. Professor Howe appeared yet to hesitate between the "beta-iron" theory and the "amorphous" theory; while apparently Mr. McCance preferred a newly-coined word, "interstrain," to any theory at all. In the verbal discussion Dr. Hatfield associated himself with the "amorphous" view. It seemed, therefore, that there was a considerable tendency to accept that view, but there were somewhat wide divergences in regard to the mode of origin or formation of the amorphous metal present in quench-hardened materials. The writer's own view at present leaned very decidedly towards the "amorphous" theory of hardening—a theory which he had had the privilege of discussing with the late M. Osmond some six or seven years ago, but he (the writer) held a somewhat different view as to the formation of the amorphous metal in a quenched material. He would, therefore, briefly discuss this question.

It would be convenient to consider first the ideas put forward by Professor Edwards, which ascribed the formation of the hard amorphous metal in quenched steel and other alloys to a highly-multiplied process of twinning supposed to take place during rapid cooling as the result of contraction stresses. The first step required to secure the acceptance of such a view was to establish the simple fact that hardened steel really did consist of intensely multiplied twinned lamellæ. Such proof had not been given, and, indeed, microscopic examination of a very large number of samples of martensite had convinced the writer that there was in that structure nothing whatever to suggest twinning. The characteristic features of twin lamellæ were a certain regularity of outline—rectilinear boundaries and repetitions of similar orientation. In martensite there were leaf-like bodies, with typically curved outlines, interlacing but without showing the least sign of repetition of orientation. In fact, it was very difficult to obtain any direct evidence of the truly crystalline character of martensite at all. It was, therefore, an assumption that martensite consisted of twinned lamellæ,

and such an assumption could only be justified if it led, without further assumptions, to a simple explanation of known facts. The second step in the theory of Edwards and Carpenter, however, required an assumption which was equally without proof, and which was in itself entirely contrary to the principles of crystallography, and also to certain observed experimental facts. This was the assumption that layers of amorphous metal were formed at the boundaries of twinned lamellæ of the same crystal. The authors of the theory apparently based this assumption on what was really a false analogy with what occurred—according to the views first put forward by Beilby—on planes of slip. On those planes there was relative *translational* movement (actual slip) between two adjacent parts of a crystal, and a profound disturbance of the arrangement of the atoms or molecules resulted. Edwards and Carpenter extended this conclusion to surfaces on which twinning took place, being apparently misled by the idea that *any* kind of internal movement must disorganize a crystal. But this is by no means necessarily the case. In slip there is relatively large linear displacement between adjacent layers of molecules or atoms, but in twinning there is nothing of the kind; the crystal elements merely rotate into a position of alternative symmetry, and there will be, as a rule, no relative displacement of the centres of gravity of adjacent molecules. Thus the process of twinning need put no strain on the internal arrangement of the crystal, particularly as the final arrangement, when twinning is completed, results in a position of equilibrium almost, if not quite, as stable as that of the un-twinned crystal. One consequence of this state of affairs is the slowness with which twinning disappears on annealing; were amorphous metal present in the boundaries of twin lamellæ, the energy stored in these amorphous layers would tend to cause coalescence of the twinned portions at a rate quite comparable with that at which crystals elongated by strain tend to coalesce. We have here one line of experimental evidence which serves strongly to support the view that twinning does not involve the formation of amorphous layers in the twin boundaries. A further line of evidence in this direction is obtained from the observations of the present writer and D. Ewen,* which showed a marked difference between the behaviour of the boundaries of twin lamellæ and the ordinary crystal boundaries when the metal is heated *in vacuo*. The deep grooves formed along the ordinary crystal boundaries, and ascribed to a consequence of the volatilization of the amorphous inter-crystalline layer present in those boundaries, were strikingly absent from all twin boundaries. Here again is evidence to show that there is no formation of amorphous layers at the surfaces of twinning. It thus appears that the twinning theory of martensite, as advanced by Edwards and Carpenter, rests upon two separate assumptions, both of which appear to be not only without any direct foundation on experimental fact, but to be directly opposed to such experimental evidence as is available. The theory may, therefore, be put on one side until its authors can bring forward direct experimental evidence in support of its fundamental assumptions.

The writer's own view of the origin of amorphous metal in material hardened by quenching has recently been expressed by him as follows† : "The gamma iron solid solution on reaching the temperature of Ar_3 begins to undergo decomposition by the formation of a large number of minute crystals of alpha iron. These minute crystals will be formed on the planes of slip and of cleavage of the gamma crystals, as some little movement must take

* Rosenhain and Ewen, "Intercrystalline Cohesion in Metals," *Journ. Inst. Metals*, 1912, ii., p. 169.

† Rosenhain, *Introduction to the Study of Physical Metallurgy* (Constable), p. 182.

place at these points, thus causing disturbance, which is favourable to transformation. Each of these extremely numerous but very minute alpha crystals will be surrounded by a film of amorphous metal which is, at any moment, in the act of passing to the growing alpha crystal and is continuously renewed from the mass of the surrounding gamma crystals. By rapid cooling, however, the growth of these alpha crystals is stopped at a very early stage, and the quenched steel is arrested in a condition in which it consists of numberless minute alpha crystals surrounded by layers of hard and strong amorphous metal, and possibly embedded in some unchanged gamma iron. The hardness of the quenched steel is then ascribable to the presence of an extremely minute network of amorphous layers. The amorphous material of these layers will not only possess the hardness of amorphous iron, but will be rendered still harder by the presence of carbide in a high state of concentration. The minute alpha crystals as they are formed must reject the carbide which was present in solution in their gamma-iron mother crystals, and this carbide will be rejected into the surrounding amorphous film."

While this view cannot and does not claim to be more than a useful working hypothesis, it has the merit of being based upon assumptions which have the support of considerable experimental evidence. The first of these fundamental assumptions is simply that every crystal—and particularly every growing crystal—is surrounded by an amorphous layer. For this assumption considerable evidence has been adduced by the work of the writer in conjunction with Humfrey and Ewen,* and although there are admittedly some who do not yet accept the existence of an inter-crystalline amorphous cement as definitely proved, there is at all events a prima-facie case for its existence. But once this assumption is granted, the rest of the theory follows as a matter of simple deduction. The hardness of the amorphous layer is admitted by the majority of those who have taken part in the present discussion, while the additional hardness due to the rejection of carbide from the growing alpha crystals can hardly be doubted. In this way the theory gives due weight to the profound effect of carbon on the hardening of steel. It is, in fact, the time occupied by this rejection of carbon that renders possible the partial suppression of the transformations by quenching.

The manner in which the theory here outlined fits most of the facts connected with hardened steel may be very briefly indicated. We have, first, the fact that if the transformation were completely suppressed, the source of hardness invoked by the theory would become inoperative. Where severe quenching, plus the restraining influence of high carbon content, is sufficient to suppress the transformation entirely at certain points, we have the appearance of austenite. With the aid of nickel or manganese the suppression can be rendered more complete, and we have austenitic steels which, while "hard" in one sense, are not hard in the sense of hardened carbon steel. Yet the austenite of these steels is strongly inclined to undergo twinning, and if extensive and minute twinning and consequent hardening resulted from contraction stresses, this type of steel should be strongly hardened. On the writer's views its relative softness is at once explained. Next, the magnetic properties of hardened carbon steel are readily explained by this theory. The ferro-magnetism resides in the numerous minute alpha crystals formed at the transformation temperature; it is probably right to suppose that the amorphous iron is more or less completely non-magnetic, but its presence in a network minutely interlacing the small alpha crystals serves to affect the

* Rosenhain, "Metals, Amorphous and Crystalline," *Engineering*, October 13, 1913. Rosenhain and Ewen, *Journ. Inst. Metals*, 1912, ii., 1913, ii. Rosenhain and Humfrey, *Journ. Iron and Steel Inst.*, 1913, i.

magnetic properties of the latter by imposing constraints upon them, in such a way as to lessen permeability and to increase retentivity. As some misconception appears to exist on this point, it may be here emphasized that the assumption that amorphous iron is practically non-magnetic is entirely consistent with the magnetic properties of cold-worked iron. Strain-hardened iron still consists very largely of crystalline alpha iron, embedded in a relatively wide network of amorphous iron. The total quantity of amorphous iron formed in the case of specimens of moderate size is probably quite small. Beilby has shown that even when extremely severely treated, the conversion of the crystalline into the amorphous phase is never even approximately completed. It cannot, therefore, be argued, as Mr. McCance appears to do, that the magnetic properties of strain-hardened iron are in conflict with the "amorphous" theory.

The form of the "amorphous" theory of hardening indicated by the author above also offers good explanations for the phenomena met with in the tempering of hardened steel. This becomes a matter of two processes which must take place simultaneously, viz. the growth of the alpha crystals and the rejection of increasing quantities of carbide from the amorphous layers as these diminish in quantity concomitantly with the growth of the alpha crystals. The former process is principally responsible for the diminishing hardness and increasing toughness of the tempered steel as the reheating temperature rises, while the latter accounts for the formation of that somewhat puzzling transition product known as troostite, which offers such striking evidences of the presence of carbide in a state of extremely fine division—the "colloidal suspension" of Benedicks.

In this connection it is interesting to draw attention to a very striking analogy in regard to "tempering" which exists between steel hardened by quenching and iron or mild steel hardened by strain. Muir * has shown that iron hardened by strain can be "let down" in stages, according to the temperature of reheating, which exhibit a striking resemblance to the stages of tempering of quenched steels. Where the analogy both in regard to hardening itself and then in relation to tempering is so complete, it is surely the most logical attitude to seek for a common cause at work in both cases. Such a common cause is offered by the "amorphous" theory.

Some reference is, perhaps, required to the "theory of beta iron." In the first place, while he himself inclines to the "amorphous" theory as outlined above, the writer would point out that the much-vaunted "burial" of beta iron was entirely premature. A vigorous attempt has been made to "talk down" the whole idea of beta iron, and in the papers here under discussion at least one writer simply states his own views on the subject—which are shared by only a few investigators—as if they were generally admitted. As against this, the work of Burgess and Crowe has established the heat-evolution at Ar_2 more firmly than ever, the causes of error which led Carpenter to deny the existence of Ar_2 in pure iron having been demonstrated. The explanation of these thermal phenomena as due to a "sudden change of specific heat" appears to the writer as entirely unsatisfactory. Even if specifically correct, it yet remains to prove to what discontinuous change in the iron this "sudden change of specific heat" is really due. The magneton theory offers an explanation, but that theory itself has yet to be established. On the other hand, it has recently been shown by Ruer † that a magnetic transition-point in at least one case is accompanied by thermal phenomena of such magnitude

* Muir, "On the Recovery of Iron from Overstrain," *Phil. Trans.*, A, 1899.
† Ruer and Kancko, *Physikalische Zeitschrift*, 1914.

that the explanation offered by the magneton theory is obviously quite inapplicable and that an "allotropic" change must be invoked.

On the other hand, it may be well to point out that the "amorphous" and the "beta iron" theory of the hardening of steel by quenching are not so much opposed to one another as might at first sight appear. In both theories it is assumed that when gamma iron decomposes at the critical temperature, before passing into the stable form of alpha iron it passes temporarily through a state in which it is neither gamma nor alpha iron, but an entirely different form. According to Mr. Humfrey's views, this transition takes place *en masse*, while in the writer's opinion it occurs only in minute layers at the surfaces of the newly-formed alpha crystals; this is a difference as to the exact mechanism, but not as to the fact itself. The amorphous theory regards this transition form as "amorphous," while the "beta-iron theory" identifies it with that form of iron stable between the temperatures of Ar_2 and Ar_3 in pure iron. It has hitherto been supposed, and there is some reason for so doing, that stable beta iron in pure iron and low-carbon steels between Ar_3 and Ar_2 is crystalline, but actual proof of this fact is not really available. On the other hand, according to Mr. Humfrey's views the metal in the transition state between gamma and alpha might be both amorphous and in the beta state at the same time. While the writer cannot see his way to accept the latter view, he quotes it in order to show that there is no vital antagonism between the two theories. He prefers, for the moment, to adopt the simple "amorphous" view because as yet there is no direct evidence to identify the transition stage in question with the stable beta phase. The evidence from the mechanical hardness of the beta phase at high temperatures is admittedly not as definite as would be required to furnish a satisfactory basis for a permanently-tenable "beta-iron theory." The position of the matter is such, however, that it is entirely premature to set the beta theory aside as definitely disproved. Professor Howe's attitude very clearly illustrates this position.

Dr. Desch refers to the recent work of Bragg on the atomic structure of crystals of copper. If the views of Bragg are correct—and it is difficult to evade the bearing of his experimental evidence—then it will become necessary to adopt entirely new conceptions as to the nature of allotropy. If the crystal is really built up, as Bragg sketches it, out of the single atoms, both of elements and also in the case of crystalline compounds, then the conception of a "molecule" existing in the solid state becomes meaningless. We have learnt to distinguish between the allotropes of sulphur, with their differences of crystalline form as "S_6," "S_8," etc., but if the crystals of all the allotropes of sulphur should really be built up of the single S atoms, then we can no longer account for the different crystalline forms by supposing a different molecular weight; we are, in fact, driven to think of allotropy as a change in the atoms themselves, and not merely in their grouping to form molecules of different sizes. If this is admitted, it is quite permissible to adopt the view put forward by Mr. Humfrey, that the amorphous metal may also exhibit allotropic changes—that, in fact, amorphous alpha iron, consisting of atoms of alpha iron, will be different from amorphous gamma iron. This is a complication of our conception of the amorphous phase which the writer is reluctant to accept unless the logic of experimental facts requires it. It is certainly a matter demanding experimental study, although the exact method of approaching the problem is not by any means obvious.

Summing up the opinions which the writer has desired to express and, as far as may be, to substantiate in his somewhat lengthy contribution, he would say that the whole question of a satisfactory and complete theoretical

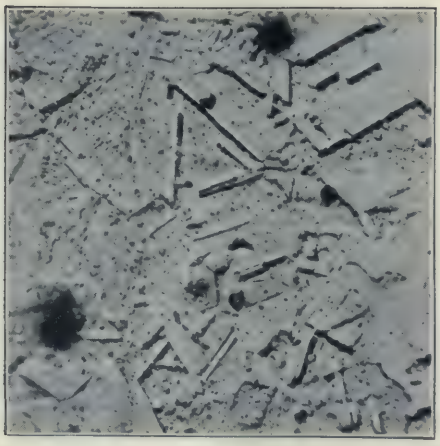


FIG. 1

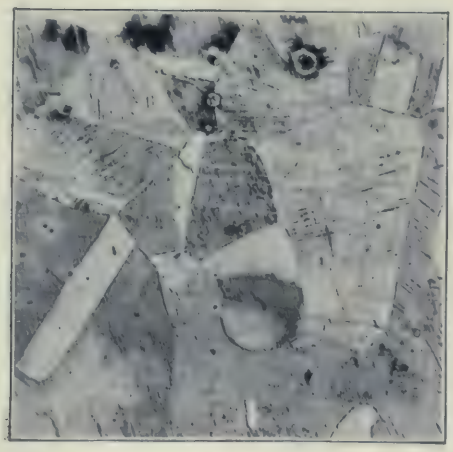


FIG. 2

FIG. 1.—Quadrant Sclerometer for Testing Hard Bars.

FIG. 1A.—Quadrant Sclerometer for Testing Soft Bars.

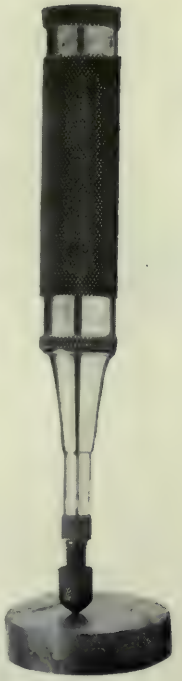


FIG. 2.

explanation of the hardening of steel by quenching has yet to be finally solved. For the moment he regards the "amorphous theory" as offering the best working hypothesis, although the final form even of that hypothesis has yet to be stated. The "twinning" theory of Edwards and Carpenter he feels obliged to reject as contrary to known facts, while he does not regard the introduction of the term "interstrain" as throwing any new light whatever on the subject.

Mr. F. C. Thompson (Sheffield, *communicated* April, 1915): Any theory which has for its object the explanation of the remarkable properties of quenched steels must be of the greatest interest to metallographers. The one recently advanced by Professors Carpenter and Edwards is certainly not the least interesting of these.

There are, however, many difficulties in the way of accepting this idea, not the least of which appears to be the fact that repeatedly twinned austenite is frequently seen whilst remaining indubitably austenite, and, for instance, non-magnetic.

Fig. 1 (facing p. 290) is a micrograph of an austenitic nickel steel, containing 33 per cent. of nickel and 0·1 per cent. of carbon. As a result of rolling at a red heat repeated twinning occurred in practically every crystal, as is readily seen despite the rather severe etching. A similar structure is often seen in the Hadfield manganese steels rendered austenitic by water toughening (Fig. 2).

Osmond and many others have published similar photographs, and twinning is so frequently present that it has been characterized as one of the chief crystalline features of alloys with γ-iron.

Twinning in austenite follows exactly the same lines as in any other solid solution, arising in practically all cases from plastic deformation, and rendered visible by crystalline growth at high temperatures. The austenitic steels as cast rarely if ever show the structure. This necessity for plastic deformation is probably one of the difficulties which has prevented the full realization of the frequency of the structure in true austenite. As one of the authors himself showed, if the work be put upon the alloy in the cold, especially if the carbon content be high, the solid solution undergoes a certain decomposition, and martensite results.

The difficulties of explaining the magnetic properties of quenched steels on this theory are great. Benedicks has shown, in a most beautiful manner, that austenite is non-magnetic, and hence the amorphous layers formed during slipping, which should approximate most closely to this condition, may be reasonably supposed to be non-magnetic also. The hypothesis advanced by McCance, that in martensite work hardened α-iron is produced as a result of the partial resolution of the solid solution, affords almost for the first time some explanation of the magnetic properties of such steels.

Demonstration by Mr. H. L. Heathcote.

At the conclusion of the meeting, **Mr. H. L. Heathcote, M.Sc.** (Coventry), showed some novel devices for testing the Hardness of Materials.

He said that the most commonly used commercial method was still the old test with a smooth file. With the object of eliminating the personal element he had devised an instrument (Fig. 1) which consisted essentially of two files and a graduated arc. The bottom file was attached to the base and could be adjusted until horizontal by the three levelling

screws attached thereto. The upper file was held down at one end by an inverted knife edge, the other end being free to move in a vertical arc. When a round article was placed in the angle between the two files and the upper arm allowed to fall slowly, the movement ceased when the forces due to friction between the files and the article were equal to the opposing forces tending to push the article out. The theory of the instrument showed that the angle at which equilibrium occurred was independent of the diameter and weight of the article, provided the coefficient of friction was the same. Since the friction depends on the amount of interlocking between the article and the projections of the file, and the interlocking on the hardness, the instrument serves to measure hardness—or more precisely it affords a measure of such properties of the metal as are, and in so far as they are, concerned in resisting the succession of changes resulting in abrasion by the files. Forms of the instrument adapted for testing heavier and non-portable articles were exhibited. In each case the principle was the same. Specially cut and hardened files were employed. Such instruments were in use for testing hardened motor and other parts, the method adopted being to set up angular limits corresponding to the various degrees of hardness required, e.g.—

Crank- and gudgeon-pins (maximum hardness)	15–20°
Twist drills, etc.	30–35°
Not hardened steel	50–70°

Another simple device was a modified automatic centre-punch in which the hardened point was replaced by a ball-holder (Fig. 2). Inside is a spring which is carefully calibrated to release the hammer at a standard pressure

Brinell Hardness No. (3,000 kg.).	Diam. (3,000 kg.).	Diam. by Auto-punch with 3-16th-inch Ball.
121	5·40	1·93 mm.
163	4·70	1·80 „
170	4·60	1·73 „
286	3·60	1·63 „
578	1·65	1·47 „

when held normally to the surface to be tested and pressed down sharply. The result is a depression similar to, but smaller than, that produced by a Brinell Hardness testing machine and is measured in the same way. The relation between the readings is indicated in the table above. Since the Brinell test applies unequal and the auto-punch equal doses of energy, and further, since the degree of mechanical hardening during the two tests may be very different, it does not follow that they should give parallel readings. The advantages of such an instrument are pretty obvious; it is portable, can be used for testing thin sheets, bars, and parts of machinery *in situ*; also for brass, bronze, delta metal, aluminium, wood, etc. New balls can be used as often as desired, as they are inexpensive and very accurately made. A solid foundation under the test piece is essential for comparative measurements. The readings indicate hardness—or more precisely they depend on and are some measure of the properties that are concerned in resisting penetration under the conditions of the test.

Such instruments, though very useful, do not supply the need (in the commercial testing of hardness) for some method of testing every part of the hardened surface. To achieve this recourse was had to baths of reagents capable of doing for hardened steel articles what the photographic developer will do for the exposed plate, viz. develop latent chemical differences.

A mixture of alcohol, nitric acid and water has been found very suitable. Clean articles immersed in such a liquid for 10 to 30 seconds are coloured a brownish-blue where the surface is martensite, and nearly black where there is troostite (due to splashing before quenching or to softening by grinding), and not appreciably changed where the surface consists of ferrite or pearlite This test is admirably adapted for the testing of large quantities of articles, e.g. after being ground to the finished size : darker or lighter patches are readily detected and such occasional specimens can be checked with a file or sclerometer.

These methods of testing had been evolved to meet the requirements of a special industry, but they had a much wider scope in other industries, and the author hoped that they might be found useful to those who, like the previous speakers, were engaged in unravelling the intricate subject of the hardening of metals.

REVIEWS OF BOOKS.

The Chemistry of Colloids and Some Technical Applications. By W. W. Taylor. (London, 1915: Edward Arnold. Pp. 328. Price 7s. 6d. net.)

This textbook appears opportunely at a time when the prospect of translations of the German works, which have so far been the only ones available, seems remote, but deserves to be welcomed quite apart from this accidental circumstance. It gives a clear and full, yet concise account of the principal facts about colloidal systems, while the discussion of theories advanced to explain these facts is kept within reasonable limits and highly controversial matter is avoided. An excellent summary—we believe the first in any textbook—is given of von Weimarn's fundamental theory of dispersoid formation, for which the author deserves the reader's gratitude, since the original papers form extremely difficult reading.

The instructions for experimental work and for the preparation of sols are such as can be successfully carried out by any careful student, the chapter on dialysis—the classical method of colloidal chemistry—being particularly good. The section devoted to Adsorption is adequate, and it is gratifying to find the author sounding a warning against the unwarranted use of the term as a description or explanation of obscure phenomena—a good many instances of which could be found in recent literature.

The applications of colloidal chemistry are illustrated by a number of varied examples sufficient to show that this discipline, while it certainly has not come to bring peace in such vexed questions as the theory of dyeing, provides a further method of attack and a large set of facts which must be taken into account in any complete consideration of the processes discussed.

One rather singular discrepancy, evidently due to an oversight, should be corrected: at the beginning of the book, Paterno's experiments on the state of tannin in different solvents are described as being of fundamental importance, while towards the end these results are (correctly) stated to be due to experimental errors.

The book is well produced, and can be thoroughly recommended to all interested in a branch of science in which so far the diffusion of knowledge has not quite kept pace with the rather general interest excited by its recent development.

An Introduction to the Study of Organic Chemistry. By H. T. Clarke, D.Sc., F.I.C. (London, 1914: Longmans, Green & Co. Pp. viii + 484. Price 6s. 6d. net.)

Whilst the number of books on Inorganic Chemistry is legion, there is no great abundance of elementary text-books on Organic Chemistry, and, as will be seen from what follows, there should be no lack of support for a work such as the above.

The usual method of introducing the subject has been considerably modified. Thus the first chapter deals with the simplest features of the chemistry of carbon compounds and the second with the more important derivatives of ethyl alcohol, as the author assumes the student to approach the subject with no previous knowledge of organic substances—an assumption which is perhaps neither justified nor necessary. In leaving out practical details the author has certainly acted rightly, for in a comparatively short text-book directions for various operations cannot be given at sufficient length to be of much use, and works dealing with the practical side of the subject should be consulted. The need for this can be readily perceived when one hears students glibly talking about various operations without having any idea as to their performance. The space thus saved is put to excellent use, for the work is rendered up-to-date by the insertion of such matter as the preparation and properties of keten and the separation of the keto- and enol- forms of acetoacetic ester. However, one would like to see the constitution of such families as the alcohols, ethers, etc., discussed at greater length, especially as the determination of constitution is so necessary a step in the synthetic production of natural bodies. The extremely important question of stereo-isomerism is well treated, and is illustrated by good diagrams. A useful chapter, not found in most text-books, is that on the mechanism of substitution in aromatic compounds.

The value of the book is greatly enhanced by a useful summary at the end, and by a well-chosen though somewhat brief set of problems. The author may find it an improvement to make the index more detailed.

The book, which has been designed to meet the new syllabus (1912) of the lower examination in Organic Chemistry in the Board of Education Examinations in Science and Technology, can safely be recommended to students of the subject as being lucidly written and providing a good introduction to more advanced Organic Chemistry.

The Chemistry of the Radio-Elements. Part I. By FREDERICK SODDY, F.R.S. Second Edition. (London, 1914 : Longmans, Green & Co. Pp. viii + 157. Price 4s. net.)

The new edition of Soddy's "Radio-Elements" has followed very quickly on the appearance of the first edition only about three years ago. It is perhaps unfortunate that the rapid development of the subject compelled the publication in 1913 of a separate section as Part II of the book, since some slight delay would have enabled the revised Part I and the recent Part II to have appeared as one complete volume. The number of radio-elements has now been increased to nearly forty, all crowded into some ten places of the periodic chart, but "there is reason to hope that something approaching completeness has now been attained with regard to these numerous and involved successive products, and though much remains to be done, it is unlikely that many more will be discovered."

Die Theorie der Strahlung und der Quanten. By A. EUCKEN. Verhandlungen auf einer von E. Solvay einberufenen Zusammenkunft. (30 Oktober bis 3 November 1911). (Halle, 1914 : Wilhelm Knapp. Pp. xii + 405. Price M. 15·60.)

This is a reminder of happier times. It is the German edition of the proceedings of the Solvay Congress at Brussels in 1911 on the Theory of Radiation and Quanta. The wide-sweeping nature of the subjects embraced by the above title is seen from the following enumeration of the separate papers

contributed to the Congress. I. H. A. Lorentz, Application of the principle of equipartition of energy. II. J. H. Jeans, The kinetic theory of specific heat according to Maxwell and Boltzmann. III. E. Warburg, Experimental tests of Planck's formula for enclosed radiation. IV. The tests of Planck's radiation formula in the region of long wave-lengths. V. M. Planck, The laws of heat radiation and the hypothesis of elementary quanta. VI. M. Knudsen, The kinetic theory and the observed properties of real gases. VII. Jean Perrin, The grounds of our belief in the real existence of molecules. VIII. W. Nernst, Application of the quantum-theory to a series of physico-chemical problems. IX. Kamerlingh Onnes, On electric resistance. X. A. Sommerfeld, The significance of quantum-action in non-periodic molecular processes in physics. XI. P. Langevin, The kinetic theory of magnetism and magnetons. XII. A. Einstein, On the present position of the problem of specific heat. Each of these papers was followed by a discussion which is briefly reported here: this report has been revised in proof by Professor Lorentz. The volume concludes with a monograph by the editor on the development of the quantum theory from the time of the Congress up till the summer of 1913.

The volume is a remarkable testimony to the rapid growth of the theory in the last few years. In spite, however, of this growth it is quite problematical as to what its final position will be. There are some who see no way of bringing theory into accord with experiment except by accepting it. There are others who find the necessary sacrifices too great and who are trying to discover some less costly way out. But whatever the final outcome of these researches may be, the development of the subject both on the theoretical and experimental sides is of vast interest, and no better account of this development exists than that presented in the present volume.

The Nature of Enzyme Action: Monographs on Biochemistry. By W. M. Bayliss, D.Sc., F.R.S. Third Edition. (London, 1914: Longmans, Green & Co. Pp. 180. Price 5s. net.)

This third edition of Professor Bayliss's very interesting Monograph on the Nature of Enzyme Action testifies to the interest which is taken in the subject of Biochemistry and to the value of the work. It would be difficult to overrate the importance of Biochemical Research—it deals with the fundamental facts of nature. Enzymic action is Nature's way of arriving at the most complex of chemical and physical reactions. It follows therefore that its study tends to elucidate and reveal the secrets of Nature and may well help the physician to combat disease. As more and more is known of enzymic reactions, so it is becoming of greater and greater value to the applied chemist.

The author first deals with catalysis in general. After giving a mechanical illustration of catalysis, that of the lessening of friction between a weight and a glass plane by the addition of oil, a definition of catalysis is given as "a substance which changes the rate of a reaction already in progress or which is capable of proceeding without supply of energy from without if certain resisting influences are removed." The next section deals with enzymes as catalysts, defining enzymes as the catalysts produced by living organisms. The activity of the enzyme catalysts is extraordinary; for example, it is computed that rennet can curdle 400,000 times its weight of caseinogen in milk. The study of such substances is most fascinating and is of great importance in the industrial world.

This book is so well known by those who have made a study of the subject that it is not necessary to review it at length, but to those who have not studied enzyme reactions this book is to be most strongly recommended, as it cannot fail to give them an interest in this branch of chemistry and will give an idea of the careful and painstaking work which has been carried out with these rather unstable catalysts.

An Introduction to the Study of Physical Metallurgy. By Walter Rosenhain, B.A., D.Sc., F.R.S. (London, 1914: Constable & Co., Ltd. Pp. 368. Price 10s. 6d. net.)

This volume is intended to be the introduction to a Metallurgical Series which is in course of publication by Messrs. Constable under the general editorship of Dr. Rosenhain. The task of writing a text-book on the physical and physico-chemical properties of metals and alloys could not have been placed in more capable and experienced hands than those of Dr. Rosenhain, and whether in the method of treatment and arrangement or the general clearness of exposition, this presentation of the subject leaves little to be desired. Of course, the book pretends to be hardly more than a survey of physical metallurgy—written from the point of view of internal structure and constitution—so vast a field has this science covered in the last few years, but the reader who has mastered it will have so clear an understanding of the subject that he will find little difficulty in applying the general principles here explained to more particular aspects, and the excellent bibliographies given at the end of every chapter will easily enable him to follow up the detailed investigations referred to broadly in the text.

After an introductory chapter, the book is divided into two main sections. Part I deals with The Structure and Constitution of Metals and Alloys. In the chapters which describe the experimental side of the microscopic examination of metals the author's wide experience is particularly evident, and the practical advice interspersed among these pages will be of value to the old hand as well as to the beginner. Thus the simple method of uniformly heating and cooling specimens by passing them along a long vertical furnace which is heated at one end only will probably be new to many a worker in metallography, and it will commend itself as a decided advance on the recognized method of varying the temperature of the furnace itself. The explanation of the Constitutional Diagram is admirably clear, although when we come to the more complex examples which are given, such as the zinc-copper and tin-copper systems, we think perhaps the author has strained his powers of compression a little too severely, and he might have explained more clearly to the beginner the experimental basis for much of the detail of the diagrams. The iron-carbon system has a chapter to itself, in which its similarity to other alloy systems is emphasized. This chapter, too, is admirably clear, although the above-mentioned reservation applies here again, if to a less degree.

The second Part of the book deals with The Properties of Metals as related to their Structure and Constitution, and contains chapters on The Mechanical Testing of Metals—an excellent summary of recent practice—the Structure of Metals under Strain, which recalls the fact that it was the important work of Professor Ewing and Dr. Rosenhain on slip bands, published in 1900, which first brought the author's name into prominence as an investigator, the Thermal Treatment of Metals, in which the processes of annealing are explained and illustrated with admirable simplicity and lucidity, and, finally, all too brief chapters on the Mechanical Treatment of Metals and

Defects and Failures in Metals and Alloys. On the question of the hardening of metals, which has lately attracted the attention of the Faraday Society, the author appears to preserve a somewhat open mind, but he inclines to accept Dr. Beilby's conception of an amorphous phase in metals, at least as produced by deformation as a result of the mechanical disruption of the crystalline arrangement of the molecules. As to the hardening of steel by quenching, Dr. Rosenhain favours a modification of Mr. Humfrey's view that the γ-iron crystals in passing the transition temperature break up into a chaotic amorphous condition and that rapid cooling prevents their rearrangement into crystals of α-iron and cementite. But so as to avoid the assumption that considerable quantities of the unstable amorphous phase are present in the steel, it is suggested that the break-down of γ-crystals only occurs in thin films around the boundaries of the growing α-crystals. Hardness is thus ascribable to the presence of a minute network of amorphous layers, which not only possess the hardness of amorphous iron but are rendered still harder by the presence of carbide in a high state of concentration. This interesting hypothesis may perhaps point the way to a reconciliation between the extreme "allotropists" on the one hand and the extreme "carbonists" on the other.

It is unfortunate that this book, so well printed and excellently illustrated, should be marred by the presence of a great many errors in the text and wrong references to diagrams. It is unnecessary to give a list of these here, but it is to be hoped that such defects will be remedied in a future edition.

The Copper Smelting Industries of Canada By ALFRED W. G. WILSON, Ph.D., Chief of the Metal Mines Division, Department of Mines, Canada. (Ottawa, 1913. Pp. 184.)

This is one of the most interesting of the remarkable series of Reports and Maps being issued almost continuously by the Department of Mines of the Canadian Government under the general editorship of its Director, Dr. Eugene Haanel. The present Report gives first a historical review of the development of the copper smelting industries of Canada, then a full description of one of the plants of each of the six great companies engaged in the industry, and finally a chapter on Statistics of Copper Production. Like all the Reports published by the Department, it is splendidly, even sumptuously, got up, and it is profusely and beautifully illustrated with maps, diagrams, and photographs. Not only this Report, but the whole series, is one of which those responsible for its issue can be justly proud. Home Departments might well imitate enterprise of this kind.

Copies of these Reports and a full list of those issued may be had on application to the Director of the Department of Mines, Sussex Street, Ottawa.

The Electrical Conductivity and Ionisation Constants of Organic Compounds. By HEYWARD SCUDDER. (London, 1914: Constable & Co. Pp. 568. Price 12s. net.)

This book contains a bibliography of the periodic literature on electrical conductivity and ionisation constants from 1889 to 1910 inclusive; from 1911 onwards the data in question are contained in the Annual Tables of Physical and Chemical Constants. The data in question are given in tables which contain references to the papers in which the work was originally described.

In addition to the general tables a formula index, a subject index, and an author list, containing over 2,000 references, are given. The writer has found the book very useful and convenient for reference. The author is to be congratulated on the completion of what must have been a very laborious and somewhat dreary task.

Tables Annuelles de Constantes et Données Numériques. Volume III. Année 1912. (London, 1914: J. & A. Churchill. Pp. lii + 595. Price 28s. net.)

The editors of the "Annual Tables" are to be congratulated on having reduced the size of the volume from 759 to 595 pages, a decrease of more than 20 per cent., without appearing to have lost anything of value in the process. These tables are becoming so indispensable to scientific workers that anything that tends to reduce the cost of production, and so contributes to their prospect of permanent survival, is heartily to be welcomed. It would be a real disaster if the complexities of the international situation were allowed to interfere with the publication of so useful a work.

Since the publication of the full book of tables it has been decided to issue certain parts of it in separate volumes, each complete in itself, and edited by its own specialist. We have received some of these parts, dealing with Electricity, Spectroscopy, Radioactivity and Ionisation, Engineering and Metallurgy, Crystallography, and Biology and Biochemistry.

Text-book on Wireless Telegraphy. By RUPERT STANLEY. (London, 1915: Longmans, Green & Co. Pp. 344, 201 figures. 7s. 6d. net.)

Clear description and an orderly presentation of the subject characterize this book. In the first eight chapters the theory of the subject is built up with the aid of clear explanations based on the conception of electric and magnetic strains in the ether, and in this part of the book especially we find Professor Stanley's work excellent: without undue labour the reader is given a really good idea of the etheric phenomena underlying the practical matters to which he is led in the later parts of the book, and this is done without the stumbling-block of advanced mathematics. Following upon a brief historical section are chapters dealing at length with coupling and transmitting and receiving apparatus and circuits, separate chapters being devoted, in due sequence, to aerials and their adjuncts, detectors, and undamped wave systems. A chapter on measurements in radio-telegraphy and four appendices conclude this very useful work.

The information given in regard to apparatus and systems is, generally speaking, up to date, and the provision of examples and questions at the end of each chapter is a useful feature which will undoubtedly assist in fulfilling the author's desire to produce a book which will meet the special requirements of those desiring to qualify as wireless operators and of the equally numerous class comprising amateurs in the subject. At the same time we feel assured that this admirable book will be of service to others who may already be in closer touch with wireless matters.

Molecular Association. By W. E. S. TURNER, D.Sc. (London, 1915: Longmans, Green & Co. Pp. viii + 170. Price 5s. net.)

The question of molecular complexity is one of great interest and importance, and the publication of a monograph on this subject in Findlay's series is therefore to be welcomed. Moreover, the author of the monograph, Dr. Turner, has himself made very useful contributions to the subject of which

he treats. The book is divided into ten chapters, one dealing with molecular associations in gases, two with the molecular complexity of dissolved substances, and three with molecular complexity in the liquid state. The remaining chapters are devoted to the discussion of the theory of dynamic allotropy, the selection and use of molecular formulæ, and molecular association and physical properties.

In most respects the author has done his work well. All the important methods used in the various branches of the subject are adequately described, and the critical discussion of the different methods is a useful feature of the book. On minor points there is room for differences of opinion, but the author's criticisms are based on a wide knowledge of his subject, and on the whole seem well founded. An appendix contains a bibliography of all the investigations on the molecular complexity of dissolved substances and a summary of the results.

The many merits of the book are marred to some extent by an unsatisfactory literary presentation. Owing no doubt partly to haste slipshod sentences abound, and in a subsequent edition the book should be carefully revised from this point of view.

Electro-Thermal Methods of Iron and Steel Production. By JOHN B. C. KERSHAW, F.I.C., with an Introduction by Dr. J. A. FLEMING, F.R.S. (London, 1913: Constable & Co., Ltd. Pp. xix + 239. Price 8s. 6d. net.)

This book, expanded from an earlier handbook published in 1907, by an author who has always kept in close touch with progress in the electrometallurgical industries, is an admirable summary of the present position in the electrical production of iron and steel. There was recently reviewed in these pages the English version of a somewhat similar handbook by Rodenhauser and Schoenawa, but these authors are identified with a particular type of furnace, whereas the present author is in the position of being able to review all the various furnaces from a purely objective standpoint, and those desirous of judging for themselves the relative advantages and drawbacks of the different types will find in Mr. Kershaw a safe and impartial guide.

The bulk of the book is naturally devoted to accounts, brought up to date, of the Héroult, Girod, Stassano, Kjellin, and Keller furnaces. An earlier chapter deals with the fairly well-known electric smelting experiments that have been made in Italy, France, Canada, Sweden, and California, and later chapters bring before the reader some of the newer and less celebrated forms of furnaces, a consideration of which is, however, of the utmost importance, for some of these may well develop into forms that are more efficient and more economical than those which now more or less hold the industrial field to themselves.

In his short but suggestive introductory chapters the author indicates some of the directions in which, in his considered opinion, future improvement and developments should be looked for. These he thinks will occur in connection with details of furnace working and control rather than in any alteration of the broad lines of furnace design, and he indicates, as the most pressing needs of the moment, the improvement of electrodes and their holders and the provision of a more durable refractory material for furnace linings than is at present on the market. With regard to the former problem, iron or steel electrodes alloyed with rarer metals are considered as likely to afford the simplest solution.

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AN ELEMENTARY ACCOUNT OF THE QUANTUM THEORY.

By J. RICE, M.A., Lecturer in Physics, Liverpool University.

(*A Paper contributed to the* TRANSACTIONS *of the Faraday Society, March* 1915.)

During the nineteenth century certain facts had been well established concerning the radiation contained in an enclosure maintained at constant temperature. Balfour Stewart and Kirchhoff had shown that if the material of the walls was not perfectly reflecting for any quality of radiation, any constituent of the radiation having a definite frequency was present in an amount depending on that frequency, the temperature and size of the enclosure, but independent of the nature of the wall-material. Stefan and Boltzmann had proved that the energy of the total radiation in one c.c. was proportional to the fourth power of the absolute temperature. Wien had reached the conclusion that the energy-density of those constituents of the radiation, whose wave-lengths lay between narrow limits λ and $\lambda + \delta\lambda$, was $\frac{f(\lambda T)}{\lambda^5}\delta\lambda$, where the function f in the numerator, although undetermined in form, was dependent on the single variable λT, the product of the wave-length and the absolute temperature. These statements had been arrived at by reasoning of a purely thermodynamic nature, based on the existence of a radiation pressure. It was only natural that the statistical methods, already employed as a successful weapon of attack on problems arising out of the kinetic theory of gases, should be presently pressed into service in this new line of research. There is some resemblance between a vessel containing molecules, individually uncontrollable but maintaining a certain average condition of energy by encounters, and an enclosure maintaining a statistically permanent condition of radiation by the emission and absorption of its walls, while the history of any particular wave-train of definite frequency cannot be followed in detail. There is one marked difference between the two cases: molecules can, by direct encounter with each other as well as by collision with the walls, exchange energy; but in a temperature enclosure passage of energy from one wave-train to another must take place through the agency of the walls alone or of matter contained within them, since two

such trains can pass through the same element of volume, i.e. cross one another without any change in the energy or quality of the trains. For this reason, if the walls are perfectly reflecting, any arbitrary condition of radiation supposed existing at one moment would remain permanently unaffected in the energy and quality of its constituents, and only by the introduction of a piece of non-reflecting matter into the enclosure could the radiation be gradually brought to the condition of "full" or "complete" radiation for the temperature, the condition considered by Balfour Stewart and Kirchhoff.

Wien, himself, had made an attempt to determine the form of the function in the numerator of his so-called displacement formula.* He considered the enclosure to contain a perfectly absorbing or "black" body, which he assumed to be a gas with its molecules distributed according to the Maxwell law, and its temperature therefore proportional to the mean squared velocity. A further hypothesis (a very doubtful one) was the assumption that those molecules whose velocities lie within certain narrow limits at a definite instant are at that instant emitting light within narrow frequency limits, with an intensity proportional to the number of those molecules. By these means Wien arrived at the form $e^{-\frac{c}{\lambda T}}$ for his function $f(\lambda T)$, c being a constant. Measurements carried out shortly after by Lummer and Pringsheim, Beckmann, and Rubens verified the formula as a good representation of the facts for short wave-lengths, but found it completely at variance with the facts for long wave-lengths.

It was by the application of statistical principles in another direction that the next advance towards a correct radiation formula was made. Wien had considered the molecules of the black body. Lord Rayleigh, and afterwards Jeans, considered the radiation itself, assigned coordinates to it and "degrees of freedom," and applied the results of Maxwell's distribution law directly to these concepts. Such applications are certainly rather easier to apprehend "physically" in the case of gas molecules than in that of constituent wave-trains of radiation; there is more "substantiality" about a molecule than a wave-train. The representation of a molecule as a small, hard sphere with perfect resilience, which is quite adequate for many purposes, and analogies with billiard-balls, discs, etc., put one on fairly familiar terms with molecular motion and exchange of energy. The degrees of freedom of such simple systems are easily calculable, being in fact six for a "rigid" molecule of any shape. Even if we introduce atomic structure into the molecules, the degrees can still be computed if one knows the parts and their connections. The energy of the system at a given temperature is then obtained by the principle of equipartition, which is derived from the law of distribution, and asserts that the kinetic energy can be calculated by assigning to each degree of freedom an amount $\frac{1}{2}kT$ ergs, where k is the molecular gas constant ($1{\cdot}35 \times 10^{-16}$ erg/degree), an equal amount of potential energy being also assigned to any degree of freedom, if there are "elastic" forces of the usual simple harmonic type.

If such ideas are to be generalized and extended to the ether of an enclosure, a definite notion as to the structure of the ether is imperative before any headway can be made in calculating its degrees of freedom. At the outset it is fairly evident that the usual conception of the ether as a perfectly continuous medium indivisible into an enumerable number of discrete parts, should lead to an infinite number of degrees of freedom, with the resulting conclusion that in a state of equilibrium the ether in the

* *Wied. Ann.*, 58, p. 662, 1896.

enclosure should contain all the energy and the walls none. The well-known illustration of the gradual loss of vibratory energy from the particles of a sounding body to the surrounding air may serve to make this point clearer. This conclusion is in fact reached by the Rayleigh-Jeans analysis, and is very much at variance with the facts as we know them. The formula arrived at, however, is a close approximation to the truth for long wave-lengths, and the calculation of the number of degrees of freedom has proved of signal service in itself. It is impossible to reproduce the analysis here, but an analogy from sound waves may serve to show the principles on which it is based. It is well known that an organ pipe will resound only to notes of definite frequencies, the fundamental and its overtones. This is due to the fact that any state of "stationary" wave-motion which will persist in the air of the pipe has to satisfy certain end conditions—e.g. at a closed end there can be no vibratory motion of the air particles, at an open end no change of pressure. Any text-book on sound shows that from these conditions there can exist in a very narrow pipe, closed at both ends or open at both ends, only waves whose wave-lengths are $2l$, $\frac{2l}{2}$, $\frac{2l}{3}$ . . . $\frac{2l}{n}$, etc., where l is the length of the pipe. The frequencies are, of course, $\frac{v}{2l}$, $2\frac{v}{2l}$, $3\frac{v}{2l}$ . . . $n\frac{v}{2l}$, etc., where v is the velocity of sound. Now if we write ν for $n\frac{v}{2l}$, we see that the number of possible modes of vibration whose frequencies are not greater than ν is $n = \frac{2l}{v} \cdot \nu$. Remembering that this is the result for a narrow pipe in which the wave-motion is parallel to one direction, let us extend the method to a flat shallow box, enclosed between two square ends so that the wave-motion takes place in any direction lying in one of the ends. The number of modes of vibration having ν as the upper limit of their frequencies would now be proportional to $\left(\frac{2l}{v} \cdot \nu\right)^2$, a result not difficult to apprehend, since we can in a rough sort of way suppose that with any one type of wave-motion parallel to one edge of the flat ends, we can compound any of the types which can exist parallel to the rectangular edges so as to obtain a possible wave-train travelling obliquely round and round the box, reflected continuously from the narrow long faces which also bound the box. If we still further extend these considerations to a cubical box, the number of possible modes come out to be proportional to $\left(\frac{2l}{v} \cdot \nu\right)^3$, i.e. to $8\frac{\tau}{v^3} \cdot \nu^3$, where τ is the volume of the box. A differentiation shows that the number of possible modes which lie between narrow limits of frequency ν and $\nu + \delta\nu$, is $24\frac{\tau}{v^3} \cdot \nu^2 \delta\nu$. As a matter of fact a complete analysis shows that the numerical factor should be 4π and not 24. Now the point of this analogy lies in the fact that whatever be the nature of a beam of radiant energy, a certain definite condition has to be obeyed at a perfectly reflecting surface—on the electromagnetic theory the tangential component of the electric intensity in the wave must be zero there—and this condition limits the number of types of radiation wave-trains which can persist unchanged as stationary waves in an enclosure with reflecting walls. Consequently, if we introduce a small portion of perfectly absorbing matter into a cube with perfectly reflecting walls, we can assert that, despite the fact that the matter can radiate and absorb any type of radiation, only those types will exist in the final state of equilibrium which satisfy the boundary conditions referred to above, just as

our box organ-pipe would not resound to every small whistle introduced into it, but only to a whistle having one of a definite series of pitches. These types of radiation will constitute complete radiation at the temperature, since experiment has certainly justified Kirchhoff's conclusion that the frequencies and energies of the constituents of radiation in a temperature enclosure are independent of the size or nature or shape of the walls, so long as there is present a portion of non-perfectly reflecting matter. The number of types of radiation, therefore, which exist in full radiation, having frequencies between the narrow limits ν and $\nu + \delta\nu$, would appear to be $4\pi \frac{\tau}{c^3} \cdot \nu^2 \delta\nu$, where c is the velocity of light; but, as a matter of fact, this number has to be doubled, since radiation waves are transverse to the direction of propagation (not longitudinal to it, as in the case of sound waves), and therefore any particular wave has to be regarded as due to the composition of two waves of the same period and phase, each polarized in one of two definite rectangular planes. So the final result for the number is $\frac{8\pi\tau}{c^3} \nu^2 \delta\nu$. This means that in order to specify the electromagnetic condition (electric and magnetic intensities) at any assigned point in the ether of the box, at any assigned instant, expressions involving a number $\frac{8\pi\tau}{c^3} \nu^2 \delta\nu$ of terms each varying harmonically with the time would be required to designate that part of the effect due to waves of frequencies in the range ν, $\nu + \delta\nu$. This number is in fact the number of independent coordinates or degrees of freedom for such qualities of radiation. Ascribing the usual kT units of kinetic and potential energy to each degree, we obtain for the energy of radiation in the range ν, $\nu + \delta\nu$, the amount $\frac{8\pi\tau}{c^3} k\mathrm{T}\nu^2 \,.\, \delta\nu$ ergs, or for the energy density, $\frac{8\pi}{c^3} k\mathrm{T}\nu^2 \,.\, \delta\nu$ ergs per c.c. In terms of wave-lengths we obtain by putting $\nu = \frac{c}{\lambda}$ and $\delta\nu = -\frac{c}{\lambda^2}\delta\lambda$, that the energy density of radiation whose wave-lengths lie in the range λ, $\lambda + \delta\lambda$ is $\frac{8\pi k\mathrm{T}}{\lambda^4}\delta\lambda$ ergs per c.c.*

It is an obvious drawback to the Rayleigh-Jeans expression that it does not approach a finite limit as λ decreases to zero. In fact, the ether would appear to contain an infinite amount of energy per c.c., since—

$$\int_{\infty}^{0} \frac{d\lambda}{\lambda^4}$$

is certainly infinite.

We might evade this objection by observing that exchange of energy from one type to another must be effected by the material of the enclosure (as was pointed out above), and that we might reasonably suppose the radiating mechanisms in the atoms to be of such a nature that they could not emit radiation of a quality higher than a certain limiting frequency, and so the upper limit of the integral would be a finite quantity and not zero. But this would not meet the difficulty that for the same amount of range in wave-lengths, $\delta\lambda$, there is a greater contribution to the energy density from high-grade qualities than from low-grade, according to the Rayleigh-Jeans formula; whereas experiment shows that the factor of $\delta\lambda$ exhibits a maxi-

* *Phil. Mag.*, 49, 539, 1900; 10, 91, 1905; 17, 229, 1909. *Nature*, 72, p. 94 and p. 243, 1905.

mum value for a certain wave-length λ_m (dependent on temperature), and approaches zero as a limit as λ approaches zero or infinity.

It has been suggested that the tendency, expressed in the Rayleigh-Jeans law, of the radiation energy to pass more and more into the higher qualities, is in reality a true phenomenon of nature, and that we fail to appreciate it in our experimental tests because all temperature enclosures fail to confine the energy of the highest frequencies; such energy leaks out, as it were, through the walls and through the small opening facing the radiometer, almost as fast as it is supplied from low-frequency radiation by the agency of the walls; and so the condition we actually observe is a compromise—a stage on the way to the final consummation expressed in the ideal formula, but unattainable except after an enormous lapse of time. The difficulty of accepting this suggestion is the difficulty of believing that such a compromise should be found to be so completely independent of the nature of the walls as experiment demonstrates. The formula, however, does agree with fact very well for long wave-lengths, just as Wien's does for short.

Faced with this discrepancy, there are two alternatives which offer themselves as obvious methods of escape from it. We may deny the validity of the calculation of the degrees of freedom, or we may urge objections to the law of equipartition of the energy. As a matter of fact, Planck's quantum hypothesis arises from his adoption of the second alternative, and a denial of the validity of equipartition in the case of vibratory motion. The principle of equipartition was first deduced in connection with the kinetic theory of gases. Now even in this original and limited sphere the principle does not stand on absolutely undebatable foundations. A great deal depends on the interpretation of the meaning to be attributed to the word "average." It is usually assumed that the average condition, say, of a molecule, is a "time" average; the sum of successive values of a quantity connected with the molecule, over a long period of change in the system, divided by the number of such values.

But it is doubtful if the principle of equipartition based on such an interpretation of the word "average" is really proved at all by dynamical principles. The point is fully treated by Jeans in his *Dynamical Theory of Gases*. It would appear that the "average" really referred to is an average extended over all conceivable conditions or "complexions" of a system (excepting a negligible number), and not merely over such conditions or "complexions" through which the system passes on any particular "path." The extension to "time" average cannot be made unless by the introduction of Maxwell's assumption of "continuity of path," viz. that the system will in process of time pass through all conceivable "complexions." This assumption is of doubtful validity, and is known to be unsound in certain of the problems treated in general dynamics, e.g. the periodic orbits of astronomy (a type of vibratory motion).

To proceed, Planck, denying the applicability of equipartition to radiation theory, works out from special considerations (to be dealt with presently) that in the vibratory motion obtaining in wave-trains, each degree of freedom corresponding to a frequency ν should possess on the average not kT ergs of kinetic and potential energy, but an amount—

$$\frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}} - 1} \text{ ergs}$$

(where h is a new universal constant, determined by experiment to be approximately $6{\cdot}55 \times 10^{-27}$). If we make use of the Rayleigh-Jeans calcula-

tion of the degrees of freedom, we find that the energy-density of the radiation in the range ν, $\nu + \delta\nu$ is—

$$\frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \cdot \delta\nu \text{ ergs per c.c.,}$$

or in terms of wave-lengths—

$$\frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda T}} - 1} \cdot \delta\lambda \text{ ergs per c.c.}$$

These expressions agree remarkably well with the most recent measurements, for all values of ν or λ, enabling the calculation of h to be made with some precision.*

It is only natural that, in adopting a more or less revolutionary attitude to a principle hitherto enjoying the confidence of the scientific world, Planck and his followers should have modified somewhat the original presentation of their ideas to meet the various criticisms urged by those who seek to retain the traditional standpoint. It is well known that Planck himself has receded somewhat from the position adopted in his earlier papers on the subject. This position is fully expounded in the first (1906) edition of his book, *Theorie der Wärmestrahlung* (Leipzig, Barth); the later form of his theory is contained in *Deutsch. Phys. Gesell. Ver.*, 13, 3, 138, 1911, or in the second (1913) edition of the above book. Einstein's speculations and applications are to be found in various papers in the *Annalen der Physik* from 1905 onwards.

It is impossible to reproduce the whole of Planck's line of argument here, but the following brief account will bring out the essentially novel principle introduced by him, and serve also to show to some extent why and how he receded from the earlier to the later position.

He remarks that any radiating mechanism of frequency ν, placed in a temperature enclosure, will acquire an average energy depending on the energy-density of the radiation of that frequency in the enclosure. The radiating mechanism of which he avails himself is an electric doublet, consisting of an electrified particle vibrating harmonically under the attraction of an oppositely electrified nucleus to which it is held by a force of the usual elastic, proportional-to-the-displacement type. In the enclosure there exist a great number N of these doublets or "oscillators," having their axes fixed in a certain direction, i.e. endowed with one degree of freedom. By an application of the usual equations of the electromagnetic field, he shows that—

$$U(\nu) = \frac{8\pi\nu^2}{c^3} L(\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $L(\nu)$ is the mean energy (kinetic and potential) of an oscillator, and $U(\nu) \cdot \delta\nu$ is the energy-density of the radiation in range ν to $\nu + \delta\nu$. Of course if we put $L(\nu)$ equal to kT, as usual, we would arrive as before at the Rayleigh-Jeans law. Planck, however, avoids this by assuming that his oscillators can only emit and absorb discontinuously, and that at any instant the energy of an oscillator can only be an integral multiple of a finite unit or "quantum" of energy, the amount of the unit depending on the frequency. It is to be carefully noted that this does not imply, of necessity, an atomic structure for energy—a view, indeed, repudiated by Planck; it does imply

* *La Théorie du Rayonnement* (Gauthier-Villars, 1912), pp. 78–92. (*This is a collection of papers bearing on Radiation and the Quantum Theory read at the Solvay Conference at Brussels in* 1911.)

that the oscillator must emit or absorb whole quanta of radiation at one time (at present, be it noted, we are discussing Planck's earlier views). Now such an assumption necessarily involves a modification of Maxwell's distribution law, for that law depends on the possibility of the infinite divisibility of the energy among the oscillators, atoms, molecules, and so forth. The point is more easily followed with aid of a "condition-diagram." Suppose we denote the charges of the doublets as $\pm e$, the mass of the vibrating particle as m, and x as its displacement along its axis at time t, then the equation of its "free" motion is—

$$\ddot{x} + 4\pi^2\nu^2 . x = 0$$

or—

$$m\ddot{x} + 4\pi^2\nu^2 . mx = 0,$$

where ν is the frequency. If X is the resolved component of the electric intensity of the field along x at time t, the equation of its forced motion is—

$$m\ddot{x} + 4\pi^2\nu^2 mx = e\,\mathrm{X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we denote the energy of the particle by ε—

$$m\dot{x}^2 + 4\pi^2\nu^2 mx^2 = 2\varepsilon,$$

or denoting its momentum by $v(= m\dot{x})$—

$$\frac{v^2}{m} + 4\pi^2\nu^2 m . x^2 = 2\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now the condition of any oscillator as regards the displacement and momentum of its vibrating particle can be clearly represented on a plane diagram by a point with coordinates x and y. All those oscillators whose energy is ε have their representative points lying on the ellipse—

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

where—

$$a^2 = \frac{\varepsilon}{2\pi^2\nu^2 . m'}$$

and—

$$b^2 = 2\varepsilon m.$$

The area of this ellipse is of course πab, i.e. $\frac{\varepsilon}{\nu}$.

The history of any oscillator can be represented by the motion of a point on this diagram, travelling along a curve, passing outward from the origin when the energy of the oscillator is increasing, and inwards when the energy is decreasing. Maxwell's law states that the number of oscillators whose displacements and momenta lie between the limits x, y and $x + \delta x$, $y + \delta y$ is—

$$\mathrm{A} . e^{-\frac{\varepsilon}{Tk}}\, dxdy \text{ (A being a constant).}$$

If we integrate this over the narrow ring in the diagram between two ellipses determined by values of the energy ε and $\varepsilon + \delta\varepsilon$, we have for the number of oscillators whose energies lie between ε and $\varepsilon + \delta\varepsilon$, the expression—

$$\mathrm{A}e^{-\frac{\varepsilon}{kT}}\,\delta\varepsilon\,\nu.$$

Of course, on the assumption of infinite divisibility of the energy, the total number of oscillators, N, should be—

$$\frac{\mathrm{A}}{\nu}\int_0^\infty e^{-\frac{\varepsilon}{kT}}\,d\varepsilon.$$

But the essence of Planck's idea is that this integral should be replaced by a convergent series. For, according to his ideas, the representative points can only be found on the ellipses corresponding to energies $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots \varepsilon_n$, etc., where ε_1 is the quantum of energy and $\varepsilon_n = n \cdot \varepsilon_1$; they will lie nowhere between these ellipses. The points will, as it were, jump from ellipse to ellipse. The areas of these ellipses are of course—

$$\frac{\varepsilon_1}{\nu}, \frac{\varepsilon_2}{\nu}, \frac{\varepsilon_3}{\nu}, \text{ etc., or } \frac{\varepsilon_1}{\nu}, 2\frac{\varepsilon_1}{\nu}, 3\frac{\varepsilon_1}{\nu}, \text{ etc.,}$$

and the various rings between them have all a common area. It is a feature of Planck's theory that he gives this area a constant value for all oscillators of any period, and denotes it by the letter "h," so that—

$$\varepsilon_1 = h\nu,$$
$$\varepsilon_2 = 2h\nu,$$
$$\varepsilon_3 = 3h\nu, \text{ etc.}$$

The integral expression N above must now be replaced by the series—

$$\begin{aligned}
N &= \frac{A}{\nu}\left[e^{-0}\cdot\varepsilon_1 + e^{-\frac{\varepsilon_1}{kT}}(\varepsilon_2-\varepsilon_1) + e^{-\frac{\varepsilon_2}{kT}}(\varepsilon_3-\varepsilon_2) + \text{etc.}\right] \\
&= \frac{A}{\nu}\left[h\nu + e^{-\frac{h\nu}{kT}}h\nu + e^{-\frac{2h\nu}{kT}}h\nu + \ldots\right] \\
&= Ah\left[1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\right] \\
&= Ah\frac{1}{1-e^{-\frac{h\nu}{kT}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)
\end{aligned}$$

If we now wish to calculate the total energy E, we see that the oscillators corresponding to the first term of the above series have no energy, those corresponding to the second have each $h\nu$, those to the third have each $2h\nu$ and so on. Hence we have—

$$\begin{aligned}
E &= Ah\left[e^{-\frac{h\nu}{kT}}h\nu + e^{-\frac{2h\nu}{kT}}2h\nu + e^{-\frac{3h\nu}{kT}}3h\nu + \ldots\right] \\
&= Ah^2\nu c^{-\frac{h\nu}{kT}}\left[1 + 2e^{-\frac{h\nu}{kT}} + 3e^{-\frac{2h\nu}{kT}} + \ldots\right] \\
&= e^{-\frac{h\nu}{kT}}\frac{Ah^2\nu}{\left(1-e^{-\frac{h\nu}{kT}}\right)^2} \\
&= \frac{Nh\nu\cdot e^{-\frac{h\nu}{kT}}}{1-e^{-\frac{h\nu}{kT}}} \\
&= \frac{Nh\nu}{e^{\frac{h\nu}{kT}}-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)
\end{aligned}$$

$$\therefore L(\nu) = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1} \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

By Equation (1) it follows that—

$$U(\nu) = \frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \quad \ldots\ldots\ldots\ldots (7)$$

an equation which agrees well with observed results, if, as has already been noted, h is put equal to $6{\cdot}55 + 10^{-27}$. It should be evident now that Planck escapes from the Rayleigh-Jeans conclusion entirely by his hypothesis of discontinuity in the exchanges of energy between the oscillators and the medium. Had he assumed that ε_1, $\varepsilon_2 - \varepsilon_1$, $\varepsilon_3 - \varepsilon_2$, etc., are infinitesimally small, he would have found for $L(\nu)$ in (6) the limit of the right-hand expression as $h\nu$ approaches zero, which is just kT, and so have arrived back at equipartition and the previous discrepancy. His essential point is, in fact, the assumption that h is finite, i.e. that the "elementary region of the condition diagram" has a finite size. So that in a sense Planck's theory is more an innovation in the method of probabilities, and need not be confined to radiation problems. This point will be touched on later.

Two obvious criticisms of this first line of argument have been advanced. First, Equation (1) is obtained by an application of electromagnetic equations which rest on the assumption of a continuous exchange of energy between oscillators and medium. But as Campbell in his *Modern Electrical Theory* (2nd edition) points out, this may not be a fatal flaw in the reasoning. Maxwell's equations may be quite true for average values of the electric and magnetic quantities involved without implying their absolute validity at al instants in the immediate neighbourhood of one oscillator, and so Equation (1 might still stand as an equality of average values, even though the discontinuity assumed by Planck existed for individual doublets and their near environment. It should be noted, however, in passing, that at a high temperature, say 2,000° C., the quantum of energy for high-grade light of the order $\nu = 10^{15}$ is 30 times as large as the average energy of an oscillator in these conditions.

The second objection is that to produce the enormously great number of qualities which are known to exist in complete radiation, we should have to postulate the existence of a very great number of oscillators of different frequencies. Now, all the evidence which we possess on the nature of atomic structure negatives such a view, nor is there any real evidence that any vibrating electron in an atom emits simple harmonic waves at all. Indeed, one of the outstanding difficulties of the Planck theory is just this difficulty of formulating a plausible physical basis for it.

There is a further difficulty awaiting us, when we seek to apply the notion of discontinuous absorption to the phenomena of ejection of electrons from the surfaces of bodies on which is incident a beam of ultra-violet light (the photoelectric effect), or a pencil of X-rays. All the evidence favours the view that a definite amount of energy has to be at least resident in the electron before it can be ejected. In the normal photoelectric effect, the energy of the electron after escape is found to have a maximum value $h'\nu - w$, where ν is the frequency of the incident light, h' a constant whose value agrees fairly closely with Planck's h, and w is a constant characteristic of the metal from which the electrons are escaping. A quite plausible hypothesis is that $h'\nu$ represents the amount of energy in the electron before its escape; of this it loses an amount w in leaving the atom against restraining forces which depend on the particular structure of the atom; and so, if it is on the surface and has not to part with still more energy in escaping from the influence of neighbouring atoms, it would retain an amount $h'\nu - w$ after

emergence. Now this appears to fit very well indeed with Planck's original assumption of the discontinuous and sudden absorption of a quantum $h\nu$, which, if ν is large enough, would supply the necessary energy for the escape of the electron from those atoms which the laws of chance brought at any definite instant into the suitable condition for absorption. But there seems to be this fatal objection to such a simple hypothesis, that the photoelectric effect has been observed *without any delay*, in cases where the intensity of the light, as calculated by the inverse square law and on the assumption of continuous propagation through the ether, could not have possibly supplied the necessary quantum to an electron in a molecule or atom in less that 10 or 15 minutes. Similar difficulties arise in connection with the secondary β-rays caused by X-rays, if one considers the energy of the X-ray pulse as uniformly distributed throughout the pulse. In fact, if one adheres to the hypothesis of discontinuous absorption, one must admit that the energy of any beam of radiation is not uniformly diffused throughout the space occupied by the beam. This is indeed roughly the manner in which Einstein escapes from the above difficulties. He has advanced the view that the energy of light is itself atomic in structure, and absorption and emission are of necessity discontinuous not because of the special structure of the oscillators, etc., but because of the nature of light itself. His view is, in reality, a quantum of *energy* view; it has already been observed that Planck's is not necessarily so; indeed, Planck dissociates himself at present from so revolutionary a hypothesis. It is noteworthy that J. J. Thomson had already been led to speculations somewhat similar to Einstein's, by considerations based on his hypothesis of Faraday tubes in the ether emanating from charged particles.* It should be noted that Thomson's view of a "filamental" structure in the ether might well be expected to lead to a different result for energy-density than that reached by Rayleigh and Jeans; for their calculation of the degrees of freedom in the ether, it will be recalled, depends on taking the ether as a perfectly continuous medium. Such a view would indeed be more like the adoption of the first of the alternatives referred to previously as methods of escape from the Rayleigh-Jeans discrepancy. In reference to such views, it must be admitted that, however useful they may be for the immediate purpose of overcoming such difficulties as those connected with the photoelectric effect and X-rays, and however well they suit the needs of radiation formulæ, they involve a return to the corpuscular theory of light, a raising of all the old difficulties of accounting for diffraction and interference on such a theory, and at present they lack a system of fundamental postulates, such as those on which stands the present edifice of dynamics and electrodynamics. Of course, there is no gainsaying that the construction of such a system may be attempted and may be successfully carried out, and Newtonian dynamics placed in the position of a good approximation to truth, but without absolute validity.

As has been already suggested, Planck meets these difficulties in a less revolutionary fashion; he abandons the hypothesis of discontinuous absorption, retaining discontinuous emission. By so doing he meets fairly successfully (though not entirely, as I hope to show presently) the objection lodged against his method of obtaining Equation (1). His new hypothesis concerning his oscillators is that they can emit only at definite instants, viz. when they contain an integral number of quanta, $h\nu$. If they contain any fraction of a quantum over an integral number, they cannot radiate. When radiation does take place, it is "catastrophic," i.e. it cannot cease until the whole energy of the oscillator has been lost. The particular number of quanta

* *Electricity and Matter* (Constable, 1904). *Phil. Mag.*, 19, 301, 1910.

possessed by an oscillator when it radiates are determined by the laws of chance, the chance of its reaching a given number being less the greater the number and the smaller the radiation-density. In fact, Planck's new line is based on three postulates :—

(*a*) In any finite time the total emission equals the total absorption.

(*b*) For small frequencies (i.e. long wave-lengths), the quanta of energy are so small that emission is practically continuous, and the ordinary dynamical and electrodynamical laws are a good approximation to the facts even for individual oscillators and their immediate neighbourhood.

(*c*) The chance of a particular oscillator emitting when arriving at a "critical" state (i.e. containing an integral number of quanta) is less the stronger the field. In particular, the chance of no emission taking place to the chance of an emission is a ratio proportional to the radiation-density.

Concerning these, (*a*) is clearly a statement of fact in a state of equilibrium ; (*b*) is a justifiable hypothesis, inasmuch as the Rayleigh-Jeans formula is suitable for experiments on long wave-lengths. As regards (*c*), the first part of it is plausible enough, but the particular statement of it in the second sentence appears to be an *a posteriori* assumption, based on the necessity of arriving at a formula (already experimentally proven) by the method employed.

To proceed to a brief outline of his new analysis, Planck replaces Equation (1) by another giving the rate of absorption of an individual oscillator in a field of given radiation-density. With the same notation as before, he finds on the basis of Equation (2) (taken to be valid for continuous absorption) that—

$$\frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} U(\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

As the right-hand expression is clearly positive, the equation refers to an increase of the oscillator energy, i.e. absorption.

Adopting the same geometrical representation of the condition of an oscillator as before, the history of an oscillator is not represented now by the leaping of a point from one to another of the "critical" ellipses corresponding to the energies $h\nu$, $2h\nu$, $3h\nu$, etc. Its behaviour follows the continuous movement of a point from the origin outwards, and a jump back to the origin when the point reaches some one of the "critical" ellipses (the particular one being a matter of chance), the outward journey being once more resumed. The number of oscillators is as before given by—

$$N = Ah \frac{1}{1 - e^{-h\nu/kT}} \quad (4)$$

but the Equation (5) for E must be altered. The energy of any oscillator is no longer, at any instant, an integral number of quanta ; all amounts can exist, and the average energy of an oscillator whose representative point is known to lie in a particular ring must be taken as the mean of the energies corresponding to the elliptical boundaries of the ring, i.e. it must be an integral number of quanta plus half a quantum. On this basis it is easy to show that (5) must be replaced by—

$$E = \frac{Nh\nu}{e^{h\nu/kT} - 1} + \frac{Nh\nu}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and therefore—

$$L(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

on the average.

Of course we cannot apply Equation (1) to this; that has been discarded, and replaced by (8); but before proceeding further it may be as well to remark that Planck's new hypothesis enables him to account for the photo-electric effect taking place without delay, even for weak light; for obviously there are at any instant a number of oscillators just within an infinitesimally small amount of energy from arrival in a "critical" state, and of these a portion will radiate almost instantaneously, or eject an electron. Thus Planck avoids Einstein's revolutionary postulate on the atomicity of energy.

We saw above that the number of oscillators whose energy lies between ϵ and $\epsilon + \delta\epsilon$ is—

$$Ae^{-\epsilon/kT} \cdot \frac{\delta\epsilon}{\nu}$$

and so the number whose representative points lie between the nth and the $(n+1)$th ellipse is $Ahe^{-(n+\frac{1}{2})h\nu/kT}$; the number whose points are in the next ring are $Ahe^{-(n+\frac{3}{2})h\nu/kT}$. That is, of all those which acquire an amount of energy between $nh\nu$ and $(n+1)h\nu$, the fraction $e^{-h\nu/kT}$ pass the $(n+1)$th "critical" state and acquire an amount of energy between $(n+1)h\nu$ and $(n+2)h\nu$. So $e^{-h\nu/kT}$ is the chance of no emission taking place, and therefore $1 - e^{-h\nu/kT}$ is the chance that an emission will take place. By postulate (c) above, we have—

$$\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \rho U(\nu),$$

where ρ is a constant to be determined, i.e.—

$$\rho U(\nu) = \frac{1}{e^{h\nu/kT} - 1} \quad \ldots\ldots\ldots\ldots \quad (11)$$

therefore by Equations (8) and (10)—

$$\rho h\nu \frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$= \frac{\pi e^2}{3m} \left(L(\nu) - \frac{h\nu}{2} \right) \quad \ldots\ldots \quad (12)$$

Now for small values of ν, $\frac{h\nu}{kT}$ is small and $L(\nu)$ approaches the value kT, $h\nu$ being therefore negligible in comparison with $L(\nu)$; so for *small values* of ν—

$$\rho h\nu \frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} L(\nu) \quad \ldots\ldots\ldots \quad (12a)$$

Now Hertz has shown that in this case (for here by postulate (b) the classical methods are applicable), the rate of emission of a vibrating electric doublet is equal to the fraction $\frac{8\pi^2\nu^2e^2}{3c^3m}$ of its own energy.* But in equilibrium the rate of emission is equal to rate of absorption, therefore Hertz's result gives us for our case—

$$\frac{dL(\nu)}{dt} = \frac{8\pi^2\nu^2e^2}{3c^3m} \cdot L(\nu)$$

and so by (12a)—

$$\rho h\nu = \frac{c^3}{8\pi\nu^2}$$

or—

$$\rho = \frac{c^3}{8\pi h\nu^3}$$

* *Wied. Ann.*, 36, p. 12, 1889.

and therefore by (11) we obtain once more—

$$U(\nu) = \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kt} - 1}.$$

Planck has thus succeeded in obtaining his radiation formula once more-but with the help of a rather artificial postulate (*c*), and also by ignoring the fact that his adoption of the electromagnetic equations necessarily implies a continuous radiation from his vibrating electric particle. Such a particle in its excursions backwards and forwards along an ever-increasing amplitude must of necessity have a motion which is not uniform, but now accelerated, now retarded, and must during such variations of its motion be radiating ; at least that is the logical conclusion from traditional views. As a matter of fact, in a series of interesting papers in the *Phil. Mag.*, dealing with the line-spectra of the elements, Bohr frankly admits this point, but makes a most ingenious use of it, taking the first step in fact towards a system of dynamics with which the behaviour of such systems as Planck's oscillators would harmonize.*

It is doubtful if Planck's work would ever have received the consideration bestowed on it, had it not happened that an ingenious application of it by Einstein to the problem of specific heats initiated a remarkable series of researches, theoretical and experimental, which showed the hypothesis of discontinuity was fruitful of good results in branches of physics and chemistry other than radiation. It is well known that while high-grade radiation is exchanged by some mechanism which is sub-atomic in nature (vibrating electrons for instance), infra-red "heat" radiation is emitted and absorbed by means of the atoms and molecules as a whole. Einstein's idea was that in a monatomic *solid* each atom has a definite frequency of vibration, which, he assumed, can be determined by optical methods (the "residual ray" method of Rubens for instance, or dispersion-formulæ). If $L(\nu)$ is the expression used previously, each atom has on the average an amount of energy $L(\nu)$ for each degree of freedom, that is, $3L(\nu)$ altogether, on the basis of Planck's work, extending to "infra-red, atom" oscillators. Hence if there are N atoms per gram-atom in the body, the atomic heat of the body would be $3NL(\nu)$ or $\frac{3Nh\nu}{e^{h\nu/kT} - 1}$. A differentiation of this expression with respect to T would give the specific heat at the temperature T (for constant volume). The result is—

$$C = 3Nk \frac{x^2 e^x}{(e^x - 1)^2};$$

where $x = \frac{h\nu}{kT}$ if x is small, i.e. if ν is small or T large, this expression approaches the value $3Nk$, which is known to be 5·95 calories, and is indeed the Dulong-Petit value of the atomic specific heat. For small values of T, however, x is large and the above expression grows smaller and smaller, ultimately approaching the limit zero as T approaches zero or x approaches infinity. That is, there should be a gradual decrease to zero of the specific heat of a solid as the temperature approaches absolute zero. This was known to be true in a general way. Further, as C is a function of $\frac{\nu}{T}$, curves connecting specific heat and temperature for various monatomic solids should be similar. In fact, for two solids whose atomic frequencies are ν_1 and ν_2, the curve for the second would be obtained from the curve for the first by maintaining the same ordinates (representing C) and altering all the abscissæ

* *Phil. Mag.*, July, September, November 1913 ; March 1914.

(representing T) in the ratio $\nu_1 : \nu_2$. A series of now famous researches were undertaken by Nernst and his pupils; details of the work will be found in papers in the *Ann. der Phys.*, 1911, p. 395, in the *Zeitsch. für Elektrochem.*, 1911 and 1912, in the *Théorie du Rayonnement*, and in Nernst's four lectures delivered at University College, London, on the solid state. The similarity of the curves was proved, while Einstein's actual expression, although following the general course of the change in specific heat with the temperature, exhibited considerable numerical discrepancies, especially at low temperatures. Nernst and Lindemann proposed an alternative formula—

$$C = \frac{3}{2} Nk \left[\frac{x^2 e^x}{(e^x - 1)^2} + \frac{\binom{x}{2}^2 e^x}{\binom{x}{e^2 - 1}^2} \right]$$

This, although in good agreement with results, was a piece of lucky guesswork, founded on no solid theoretical basis. In a paper in the *Ann. der Phys.* (39, p. 789, 1912), Debye attacked the problem from a broad standpoint, and his result, from its agreement with experiment and the soundness of its premises, seems to have approached finality in this domain.

Debye points out that there can be no single "characteristic" vibration of the atoms of a monatomic solid. There are an enormous number of such vibrations; they constitute an "acoustic" spectrum; they are the fundamental and overtones of the body considered as emitting a note. A knowledge of the elastic constants of the material is sufficient to determine them, just as Rayleigh and Jeans determined the frequencies possible in a cubical "block" of ether. For these vibrations constitute waves of "sound" travelling through the body with definite speeds. There are, for instance, "distortional" transverse waves travelling with a velocity v_1, and "compressional" longitudinal waves travelling with a velocity v_2. v_1 can be calculated if one knows the density ρ and modulus of rigidity μ of the material; it is in fact $v_1 = \sqrt{\frac{\mu}{\rho}}$; v_2 can be calculated if one knows in addition the bulk-modulus K—

$$v_2 = \sqrt{\frac{K + \frac{4\mu}{3}}{\rho}}.$$

Now, the number of degrees of freedom for vibrations having frequencies between ν and $\nu + \delta\nu$ is, as previously, $\frac{8\pi}{v_1^3} \nu^2 \delta\nu$ per unit volume for the transverse waves, and $\frac{4\pi}{v_2^3} \nu^2 \delta\nu$ for the longitudinal. (N.B.—The factor 8π occurs because the transverse waves are polarizable in two rectangular planes, the longitudinal are not.) Consequently the whole modes of vibration per unit volume between ν and $\nu + \delta\nu$ are $\left(\frac{8\pi}{v_1^3} + \frac{4\pi}{v_2^3}\right)\nu^2 \delta\nu$. We saw above that the similar formula developed for the ether by Rayleigh and Jeans suffered from the drawback that, in integrating it, no finite upper limit could be assigned on account of the assumed continuity of the ethereal medium. In this case, however, there must be a finite upper limit to ν because the number of degrees of freedom cannot exceed 3N for a gram-atom of the substance.

Hence if ν_m is the highest frequency possible—

$$3N = \left(\frac{8\pi\tau}{v_1^3} + \frac{4\pi\tau}{v_2^3}\right)\int_0^{\nu_m} \nu^2 d\nu$$

(where τ is the volume of a gram-atom)

$$= \left(\frac{8\pi\tau}{3v_1^3} + \frac{4\pi\tau}{3v_2^3}\right)\nu^3{}_m$$
$$= F\nu^3{}_m$$

where F is a constant calculable from the elastic constants and density of the body.

Since $\nu_m = \left(\frac{3N}{F}\right)^{\frac{1}{3}}$, ν_m is also calculable. For Al, Cu, Zn, Ag, Pb, Diamond it is of the order 10^{12} to 10^{13}.

Now by ascribing, according to the extension of Planck's work, the energy—

$$\frac{h\nu}{e^{h\nu/kT} - 1}$$

to every degree of freedom, we obtain for the energy-content of body due to wave-motion of frequencies ν to $\nu + \delta\nu$—

$$3F \cdot \frac{h\nu^3\delta\nu}{e^{h\nu/kT} - 1}$$

or—

$$\frac{9N}{\nu^3{}_m} \cdot \frac{h\nu^3\delta\nu}{e^{h\nu/kT} - 1}.$$

Hence the total energy—

$$= \frac{9N}{\nu^3{}_m}\int_0^{\nu_m} \frac{h\nu^3 d\nu}{exp\frac{h\nu}{kT} - 1}$$

$$= \frac{9NkT}{x^3}\int_0^x \frac{y^3 dy}{e^y - 1}$$

where—

$$x = \frac{h\nu_m}{kT}, \text{ and } y = \frac{h\nu}{kT}.$$

A differentiation of this expression with regard to T produces this expression for the specific heat at constant volume—

$$C = 3Nk\left[\frac{12}{x^3}\int_0^x \frac{y^3 dy}{e^y - 1} - \frac{3x}{e^x - 1}\right]$$

This is clearly a function of x or $\frac{h\nu_m}{kT}$, and therefore suitably accounts for the similarity of the specific heat curves of different solids. Further, the

expression agrees remarkably well with determinations of Nernst and his co-workers, more so in fact if ν_m is calculated not from the values of elastic constants, but from a formula discovered by Lindemann,* connecting ν_m and the melting-point (taking ν_m as the frequency of vibration of an atom under the influence of its neighbours). The computation is not easily carried out, for the integral in the above expression cannot be evaluated in finite terms, and so one has to resort to the summation of series which can be obtained to suit various ranges of temperature as regards their convergency. One striking result emerges from the calculation, viz. that at very low temperatures the specific heat varies as the cube of the absolute temperature; this would appear to be true to within 1 per cent. for the range of temperature 0° to $\frac{h\nu_m}{12k}$.

Nernst has made a very happy combination of Einstein's and Debye's formulæ in the treatment of diatomic solids such as KCl, NaCl, AgCl, KBr, and the triatomic substance $PbCl_2$. He supposes the heat content of the body to be constituted of two parts, one due to the vibrations of the molecules as a whole, and the other to the vibrations of the atoms within the molecules. The first part can be obtained by Debye's method, taking the upper limit of the frequency as determined by Lindemann's melting-point formula; the second part can be determined by Einstein's method, the characteristic frequency being determined by Rubens' "residual rays" method. The agreement with observation is quite good; details can be found in *Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (Teubner). Still further extensions of Debye's ideas have been made by Born and Kármán and Thirring in papers contained in the *Phys. Zeit.* 14 (1913).

It was pointed out above that Planck's formula is derived from an innovation in the treatment of statistical problems, the assumption, in fact, that the elementary region of the two-dimensional condition diagram for a system of oscillators is finite in area, and the replacement of Maxwell's integral by a series. Planck has applied the same idea to the six-dimensional condition diagram for an ideal monatomic gas, and arrived at a result which had been already obtained by Nernst, who bases his derivation of it on his well-known "heat theorem."† There are several ways of wording this theorem, according to the particular thermodynamic function which one elects to make use of in the statement. As expressed by Planck in his *Thermodynamics*, it is as follows: "The entropy of a condensed system, which is chemically homogeneous, is zero at the absolute zero of temperature." This law removes from the expression for the entropy of a body in a definite state that indefiniteness in value which arises in the usual thermodynamic treatment and which is due to the entrance into the formula of an undetermined constant on integrating the differential of the entropy. For clearly if the entropy of a body can be given definitely for one state, it is determinate for all other states which can be conceivably reached from the former by a reversible path. So if we can conceive that the body can be led to the condition of a chemically homogeneous solid or liquid at absolute zero, by a reversible process, Nernst's heat theorem makes it possible to calculate its entropy without ambiguity, if sufficient experimental data are available. By such means it can be shown that the entropy of one gram-molecule of an ideal gas is given by the equation—

$$S = C_p(1 + \log T) - R \log p + a \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

* *Physikalische Zeitschrift*, 11, 609 (1910).
† *Nachr. d. Ges. d. Wissensch zur Göttingen Math. Phys. Kl.* 1906).

(absolute units of temperature, pressure, and energy being used), where the "chemical constant," a, indeterminate on pure thermodynamical grounds, has, according to Nernst's theorem, the value—

$$R\log\left(\frac{p_s}{\theta^{\frac{5}{2}}}\right)+\frac{r_o}{\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which p_s is the vapour pressure of liquid condensed from the gas at a very low temperature θ, and r_o is the heat of vaporization of the liquid at absolute zero.

Planck arrives at this result on dynamical grounds in the following manner. Conceiving a monatomic gas as an aggregate of particles with three effective degrees of freedom, and representing the co-ordinates of a particle by x, y, z, and its velocity-components by u, v, w, the condition diagram is a six-dimensional one in which the position and momentum of a point representing a particle are given as x, y, z, mu, mv, mw (m being the mass of a molecule). According to the Maxwell law the number of molecules whose representative points lie within the limits x, y, z, mu, mv, mw, and $x+dx$ . . . $m(w+dw)$, is—

$$NAe^{-\frac{\epsilon}{kT}}\,dx\,dy\,dz\,du\,dv\,dw \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where N is number of molecules in a gram-molecule, ϵ the energy of a molecule in condition xyz, u, v, w, due to its position and velocity, and A is a number given by the equation—

$$1=A\int e^{-\frac{\epsilon}{kT}}\,dx\,dy\,dz\,du\,dv\,dw.$$

If one puts $\epsilon=\frac{1}{2}m(u^2+v^2+w^2)$, it follows that—

$$A=\frac{1}{V}\cdot\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}$$

V being the volume of the gas.

Now according to Planck's view, instead of the differential element of the six-dimensional diagram which occurs in (15), we ought to introduce a finite element having a value G, definite in size for a system of definite molecules. The form and position of these "elementary regions" would, as in the two-dimensional case, be bounded by the "surfaces" or loci of equal energy. If we number these regions 1, 2, 3, . . . n, we can say that a fraction f_1 of the representative points lie in region 1, etc., f_n in region n, where—

$$f_n=A\,.\,e^{-\frac{\epsilon_n}{kT}}\cdot\frac{G}{m^3}$$

ϵ_n being the molecular energy corresponding to the nth region. With this notation, it is possible to express the entropy of the gas, as Boltzmann has shown (see his *Gastheorie*, or Jeans' *Dynamical Theory of Gases*), in the form—

$$S=-kN\Sigma f_n\log f_n.$$

Of course in Boltzmann's treatment, as in Maxwell's, f_1, f_2, etc., are infinitesimally small, since the differential element $dx\,dy\,dz\,du\,dv\,dw$ occurs instead of $\frac{G}{m^3}$, and so the expression for S contains a constant of indeterminate (and infinite) value. By assuming G to be finite, Planck avoids this

conclusion, just as he avoids the Rayleigh-Jeans law in radiation, by assuming h to be finite and not infinitesimally small. He finds, by using the values given above for A and f_n, that—

$$S = kN\left[\log \frac{V(2\pi mkT)^{\frac{3}{2}}}{G} + \frac{E}{NkT}\right]$$

where E is the kinetic energy of the molecules

Writing R for k . N and putting E equal to $\frac{3}{2}$ RT, we obtain—

$$S = R\left[\frac{3}{2}(1 + \log T) + \log V + \frac{3}{2}\log(2\pi mk) - \log G\right] \quad . \quad . \quad (16)$$

Since $pV = RT$ and $c_p = \frac{5}{2}R$, Equation (13) can be readily transformed to—

$$S = R\left[\frac{3}{2}(1 + \log T) + \log V - \log R + \frac{a}{R} + 1\right] \quad . \quad . \quad . \quad (17)$$

The formal similarity between (16) and (17) is obvious, and the two results lead to the connection between Planck's G and Nernst's "chemical constant," a, given by the equation—

$$\frac{3}{2}\log(2\pi mk) - \log G = -\log R + \frac{a}{R} + 1,$$

or—

$$G = \frac{R(2\pi mk)^{\frac{3}{2}}}{e^{\frac{a}{R}+1}}.$$

The thermodynamic treatment can be found in the third edition of Planck's *Thermodynamics*, chapter vi. The development of the ideas based on the quantum hypothesis is given in his *Theorie der Wärmestrahlung* (2nd edition, pp. 110–132).

ON VON BABO'S LAW AND KIRCHHOFF'S EQUATION FOR THE LATENT HEAT OF DILUTION

By ALFRED W. PORTER, D.Sc., F..R.S

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

In deriving von Babo's law connecting the vapour pressure π of a dilute solution with the vapour pressure π_0 of the pure solvent at the same temperature, it is customary to make approximations throughout the course of the investigation which leave one at the end in a state of uncertainty as to the degree of accuracy of the final result. It seems desirable, therefore, to proceed as far as possible without making any approximation, even though the exact equations thus obtained are much more than sufficient in the present state of our experimental knowledge of ordinary solutions. These expressions, moreover, become necessary as the critical point is approached, for the usual approximations cannot then be considered good enough. There is therefore need that they should be developed in order to prepare the way for these more complicated cases.

The following notation will be employed :—

H, the latent heat of reversible dilution, i.e. the heat that must be taken in to keep the solution at constant temperature T and pressure p when 1 gram of the solvent at the same temperature and at the pressure p_0 is added *through a semi-permeable membrane* to a large quantity of it.

H_i, the internal latent heat of dilution, i.e. the increment of specific energy of the system when the solution is diluted as above. In the case of incompressible solutions this will not differ appreciably from the irreversible latent heat of dilution or heat absorbed when 1 gram of solvent is simply stirred into a solution, both being at the same temperature and *pressure*. This similarity in value is due to the very small amount of external work done by the system during such mixture.

π_0, π_π, the principal saturation pressures of solvent and solution respectively, i.e. the values when the liquids are under the pressures of their vapours alone.

u_{p_0}, specific volume of the solvent at pressure p_0.

s_p, increase of volume of solution at pressure p when 1 gram of solvent is added to a large quantity of it. The suffixes may be dropped whenever the meaning is otherwise clear.

P, osmotic pressure $= p - p_0$.

Special terms are defined when they occur.

The following general theorems may be recalled : Heat that enters unit

mass of fluid (liquid or gas) when its pressure is increased at constant temperature is—

$$-T\left(\frac{\partial v}{\partial T}\right)_p dp,^*$$

where v is the specific volume. The corresponding increase in the specific energy is obtained by subtracting from the above the external work pdv (or $d(pv) - vdp$), leaving—

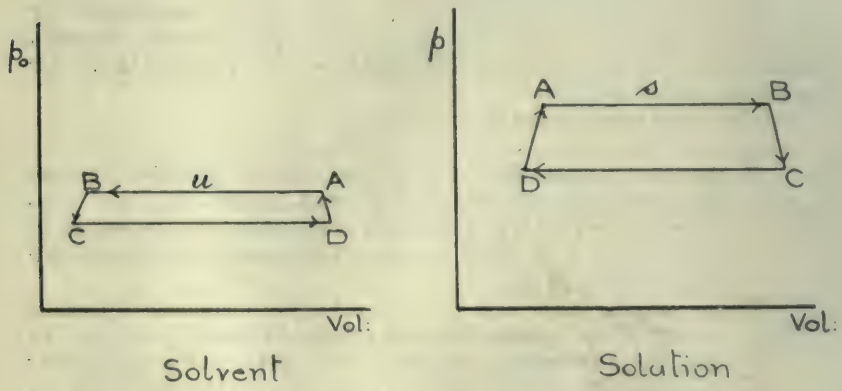
$$-\left(T\frac{\partial v}{\partial T} - v\right)dp - d(pv)$$

or—

$$-T^2\frac{\partial}{T}\left(\frac{v}{T}\right)dp - d(pv).$$

The exact equation for H is easily obtained by means of a cycle similar to that employed to prove Clapeyron's equation for the connection between latent heat and vapour pressure.

Take a large (strictly, infinite) amount of a solution at pressure p in osmotic equilibrium with the pure solvent at pressure p_0. It is convenient to represent the changes of pressure of solution and solvent on separate diagrams.



Let the solution and solvent be initially in the state A. Transfer unit mass of solvent into the solution at constant temperature T through the osmotic membrane; the solution increases in volume by s, the solvent diminishes by u; both are thereby brought to the state B. Lower the temperature of both infinitesimally to $T - dT$ without any passage of liquid across the membrane. One or both the pressures must be adjusted during the change, for the osmotic pressure $(p - p_0)$ varies with temperature. Let the new states be given by the points C. Remove the unit mass of solvent at constant temperature from the solution, through the membrane, thus bringing each to the state D. Warm to original temperature T, thus changing pressures to their old values p and p_0, and bringing the system back to its original state A.

This cycle is a perfectly reversible one, and its mechanical efficiency may be equated to the universal value dT/T.

* Preston, *Theory of Heat*, Chap. VIII, Ex. 9.

The external work done is equal to the difference of the two areas ABCD, for they are traversed in opposite senses. This difference is—

$$s\frac{\partial p}{\partial T}dT - u\frac{\partial p_o}{\partial T}dT.$$

The heat taken in at the higher temperature T is H, i.e. the reversible latent heat of dilution at that temperature ; and the efficiency is therefore—

$$\frac{s\frac{\partial p}{\partial T}dT - u\frac{\partial p_o}{\partial T}dT}{H} = \frac{dT}{T},$$

whence—

$$H = T\left(s\frac{\partial p}{\partial T} - u\frac{\partial p_o}{\partial T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This very simple expression is an exact one, even for compressible liquids. Its connection with the osmotic pressure P is shown by making use of the definition of osmotic pressure—

$$P = p - p_o,$$

and writing it—

$$H = T\left(s\frac{\partial P}{\partial T} + (s-u)\frac{\partial p_o}{\partial T}\right).$$

The internal latent heat of dilution H_i can be obtained by subtracting the osmotic work $ps - p_o u$, giving the exact equation—

$$H_i = T^2\left\{ s\frac{\partial}{\partial T}\left(\frac{p}{T}\right) - u\frac{\partial}{\partial T}\left(\frac{p_o}{T}\right)\right\},$$

in obtaining which use is made of the relation—

$$T^2\frac{\partial}{\partial T}\left(\frac{p}{T}\right) = T\frac{\partial p}{\partial T} - p.$$

Now, as is well known, the osmotic pressure can be connected with the vapour pressures of solvent and solution. It was shown by the author in 1907* that the exact relation is—

$$\int_{\pi_\pi}^{p} sdp - \int_{\pi_o}^{p_o} udp_o = \int_{\pi_\pi}^{\pi_o} vd\pi,$$

in which the second integral on the left is zero when the solvent is under the pressure of its own vapour alone.

It is at this stage that it is convenient to introduce approximations and special values.

(i) Let the solvent be under the pressure of its own vapour $p_o = \pi_o$.

(ii) Let $s - u$ be treated as negligible compared with u, as it always may be for ordinary aqueous solutions.

(iii) Let s and u be considered independent of pressure.

* *Roy. Soc. Proc.*, A, 79, p. 519 (1907).

We may then write—

$$H = Ts \frac{\partial P}{\partial T},$$

$$H_i = T^2 s \frac{\partial}{\partial T}\left(\frac{P}{T}\right)$$

$$s(p - \pi_\pi) = \int_{\pi_\pi}^{\pi_o} v d\pi,$$

and—

$$p = \pi_o + P.$$

If the ordinary gas law be accepted for the vapour, the integral is equal to—

$$RT \log \frac{\pi_o}{\pi_\pi},$$

where R is the characteristic constant for the vapour; and neglecting $s(\pi_\infty - \pi_\pi)$ we have—

$$Ps = RT \log \frac{\pi_o}{\pi_\pi},$$

whence—

$$H_i = T^2 s \frac{\partial}{\partial T}\left(\frac{R}{s} \log \frac{\pi_o}{\pi_\pi}\right).$$

Kirchhoff's equation is at once obtained from this by taking s and R independent of the temperature.*

Alternative Treatment.

An alternative mode of derivation, in which the osmotic pressure does not explicitly enter, is to calculate the change in the internal energy on evaporating from the solution and subsequently condensing into pure solvent. Take a large quantity of solution under the pressure of its own vapour π_π, and evaporate 1 gram at constant pressure and temperature. The heat entry is—

$$L_c = T(v_\pi - s_\pi)\frac{\partial \pi_\pi}{\partial T} \text{ (Clapeyron's equation)},$$

and the change in internal energy is obtained by subtracting the external work $(v_\pi - s_\pi)\pi_\pi$, leaving—

$$T^2(v_\pi - s_\pi)\frac{\partial}{\partial T}\left(\frac{\pi_\pi}{T}\right)_{\text{sat.}}.$$

Change the pressure of the vapour at constant temperature to π_o (the saturation value for the pure solvent) :—

Heat entry—

$$= -\int_{\pi_\pi}^{\pi_o} T\left(\frac{\partial v}{\partial T}\right)_p d\pi;$$

* I hope that I shall not be charged with approval either of Kirchhoff's equation or of the perfect gas law used in deriving it. As on a previous occasion I was so charged, let me say, once for all, that the above equation is now derived solely with the object of emphasizing the approximations to which it corresponds.

work done—

$$\int_{\pi_\pi}^{\pi_o} \pi dv = \pi_o v_{\pi_o} - \pi_\pi v_\pi - \int_{\pi_\pi}^{\pi_o} v d\pi ;$$

change in internal energy—

$$= - \int_{\pi_\pi}^{\pi_o} T^2 \frac{\partial}{\partial T}\left(\frac{v}{T}\right) d\pi - \pi_o v_{\pi_o} + \pi_\pi v_\pi .$$

Condense vapour into pure solvent :—

Heat entry—

$$= - T(v_{\pi_o} - u_{\pi_o}) \frac{\partial \pi_o}{\partial T} ;$$

change in internal energy—

$$= - T(v_{\pi_o} - u_{\pi_o}) \frac{\partial}{\partial T}\left(\frac{\pi_o}{T}\right)_{sat.}.$$

The *decrease* in the internal energy is equal to the internal latent heat of dilution, for its value is independent of the path of change ; that is—

$$H_i' = T^2(v_{\pi_o} - u_{\pi_o}) \frac{\partial}{\partial T}\left(\frac{\pi_o}{T}\right)_{sat.} - T^2(v_{\pi_\pi} - s_{\pi_\pi}) \frac{\partial}{\partial T}\left(\frac{\pi_\pi}{T}\right)_{sat}$$

$$+ \int_{\pi_\pi}^{\pi_o} T^2 \frac{\partial}{\partial T}\left(\frac{v}{T}\right)_p d\pi + \pi_o v_{\pi_o} - \pi_\pi v_\pi .$$

This equation is exact for this particular latent heat. It differs in meaning from the previous value H_i, because in this case it is the change of energy in passing from solvent to solution, *both being under the pressure of their own vapours alone ;* while in the former case H_i was the value when the solution was higher in pressure than the solvent by an amount equal to the osmotic pressure. As the liquids considered become more and more incompressible H_i and H_i' tend to equality.

In a similar way the equation can be obtained which suits the more ordinary conditions, viz. that the solution and solvent are under a pressure of one atmosphere or thereabout.

We may approximate to H' (i) by neglecting u and s ; (ii) by assuming vapour to follow the perfect gas law, whence—

$$v = \frac{RT}{\pi},$$

$$\pi_o v_{\pi_o} = \pi_\pi v_\pi,$$

and—

$$\frac{\partial}{\partial T}\left(\frac{v}{T}\right) = 0.$$

H_i becomes—

$$T^2\left[v_{\pi_o} \frac{\partial}{\partial T}\left(\frac{\pi_o}{T}\right) - v_{\pi_\pi} \frac{\partial}{\partial T}\left(\frac{\pi_\pi}{T}\right)\right],$$

or—

$$H_i = RT^2 \frac{\partial}{\partial T}\left(\log \frac{\pi_o}{\pi_\pi}\right)$$

which is Kirchhoff's equation once more.

To obtain a better approximation we may take the vapour equation to be of the form—

$$v - b = \frac{RT}{p} - c.$$

Callendar has shown that for water vapour throughout the range with which we are at present concerned b may be taken as 1 c.c., and c a function of the temperature alone, which he takes as varying inversely as the 10/3 power of the absolute temperature. The value of c is nearly independent of pressure for moderate values of the pressure.* It may be pointed out that this equation is equivalent to retaining the rectangular-hyperbolic form for the isotherms on a pv-diagram, as in the case of a perfect gas, but with the values of the volumes corresponding to any value of p on a given isotherm decreased by the amount c-b. At less moderate pressures c cannot be taken as independent of the pressure, so it is not surprising that the equation gives no indication of critical phenomena; as is evident from the fact that there are no kinks in a rectangular hyperbola. The values of c which he gives are—

Temp. ° C.				c (in c.c.).
0	...	...	...	74·43
20	...	...	...	58·81
40	...	...	...	47·19
60	...	...	...	38·68
80	...	...	...	31·60
100	...	...	...	26·30

The value of R he takes as ·11030 $\frac{\text{cal.}}{\text{gr. deg. C.}}$

Using this equation we will also put $u = s = b$. Then—

$$H_i' = \left(\frac{RT}{\pi_0} - c\right)\frac{\partial}{\partial T}\left(\frac{\pi_0}{T}\right) - \left(\frac{RT}{\pi} - c\right)\frac{\partial}{\partial T}\left(\frac{\pi}{T}\right)$$

$$- \frac{\partial}{\partial T}\frac{c-b}{T}\cdot(\pi_0 - \pi) + \frac{\pi_0}{T^2}\left(\frac{RT}{\pi_0} - c + b\right) - \frac{\pi}{T^2}\left(\frac{RT}{\pi} - c + b\right),$$

which on collecting the various terms reduces to—

$$\frac{H_i'}{T^2} = R\frac{\partial}{\partial T}\left(\log\frac{\pi_0}{\pi}\right) - \frac{\partial}{\partial T}\left(\frac{c(\pi_0 - \pi)}{T}\right).$$

If we apply Callendar's equation also to the value of H calculated by the former method, we have first—

$$(P + \pi_0 - \pi)s = \int_{\pi}^{\pi_0} v\,d\pi = \int_{\pi}^{\pi_0}\left(\frac{RT}{\pi} - c + b\right)d\pi = RT\log\frac{\pi_0}{\pi} - c(\pi_0 - \pi),$$

where $(b - s)(\pi_0 - \pi)$ is finally neglected. Thence—

$$H = Ts\frac{\partial P}{\partial T} = T\frac{\partial}{\partial T}\left\{RT\log\frac{\pi_0}{\pi} - c(\pi_0 - \pi)\right\},$$

and—

$$H_i = T^2 s\frac{\partial}{\partial T}\left(\frac{P}{T}\right) = T^2\frac{\partial}{\partial T}\left[R\log\frac{\pi_0}{\pi} - c\frac{\pi_0 - \pi}{T}\right].$$

* Or rather for moderate densities.

Here s is considered independent of temperature as before. This equation, to the degree of approximation obtained, is identical with the value of H_i' derived above.

If the value of H_i is zero *at all temperatures*—

$$R \log \frac{\pi_o}{\pi} - c\frac{(\pi_o - \pi)}{T}$$

is constant.

Von Babo's law is obtained by neglecting the variation of the second term with temperature. For the law to be true, then, to the accuracy of the above equation—

$$\frac{H_i'}{T^2} = -\left(1 - \frac{\pi}{\pi_o}\right)\frac{\partial}{\partial T}\left(\frac{c\pi_o}{T}\right).$$

The value of $\frac{c\pi_o}{T}$ for water vapour at 60° C. is 1·7 and at 80° C. is 3·2. Hence $\frac{H_i'}{T^2}$ would need to be—

$$-\left(1 - \frac{\pi}{\pi_o}\right) \times \frac{1{\cdot}5}{20} \times 13{,}300$$

$$= -\left(1 - \frac{\pi}{\pi_o}\right) \times 1{,}000 \text{ ergs/(deg. C.)}^2,$$

or, since $\frac{\pi}{\pi_o}$ is less than unity, H_i' would need to be negative.

If, on the other hand, H_i' is independent of temperature—

$$R \log \frac{\pi_o}{\pi} - c\frac{(\pi_o - \pi)}{T} = -\frac{H_i}{T} + \text{const.}$$

On the Physical Meaning of Kirchhoff's Equation.

So far I have treated the question purely from the thermodynamical standpoint. Useful though such an examination is, yet the physicist cannot stop here. The further question as to the mechanism which may account for the observed facts insistently obtrudes itself.

The kinetic theory of matter, which until recently was a speculation only, has become an experimental fact owing to the researches of Perrin and others on "molecular reality" and Brownian motion. We need no longer, then, have any hesitation for the case of very dilute solutions (in which the solute molecules are so far apart on the average as to exert no sensible attraction on one another) in applying the same equation as for a similar *gas*, viz.—

$$P(v - b) = RT,$$

where v = volume containing 1 gram of solute and P is the osmotic pressure. Take now our nearly exact equation for H_i, viz.—

$$H_i = T^2 s \frac{\partial}{\partial T}\left(\frac{P}{T}\right),$$

and we obtain $H_i = 0$, since—

$$\frac{P}{T} = \frac{R}{v - b}.$$

Thus in this case there would be no heat of dilution; at least, this is so provided that the molecular weight of the solute keeps constant (i.e. R = const.).

This will not keep so if there is association or dissociation of solute molecules, either with themselves or with solvent molecules (provided in the latter case that the union is of the same permanent or subpermanent character as in the former—such, in fact, that the combination moves about as a physical unit). Such a change in association alters the molecular weight and therefore the value of R, which varies inversely as it. In consequence $\frac{P}{T}$ would no longer be independent of temperature. It is unlikely, however, that when the solution is so dilute as to make the solute molecules independent of each other, as supposed, that any further separation of these molecules should cause any change in their character.

When the molecules are so crowded that one can no longer neglect the forces between them, we must copy what Hirn did for gases,* and write—

$$(P + K)(v - b) = RT,$$

where K is the so-called internal pressure due to molecular attractions. If K, as well as R, is independent of temperature, we obtain—

$$H_i = T^2 s \frac{\partial}{\partial T}\left(\frac{P}{T}\right) = Ks.$$

Hence the internal latent heat of dilution would represent simply the work done against molecular forces during the dilution.† This might, so far as we know *a priori*, be either positive or negative, because we cannot state offhand whether the solute molecules attract or repel one another when in the body of the solution. It must not be forgotten that the action is a differential one; for as soon as the volume of the molecule is taken into account it can only be present by displacing one (or more or less) solvent molecule. If the attraction between the displaced solvent and a solute molecule is greater than between the two solute molecules, the effective action will be a repulsion; in other cases it will be an attraction or nil. The fact that in the case of sugar in water the latent heat of dilution is fairly small renders plausible the supposition that this differential action is only small. On the other hand, it may be that in measuring the heat of dilution we are only observing a balance of effects arising in part from separation of the distances between solute molecules, and in part from change of association of these with each other or with solvent molecules. In this connection I may state that Lord Berkeley's values of osmotic pressure at constant temperature are fairly well represented by a formula $P(v - b) = \text{constant}$, which would seem to imply (since K is absent) that the differential attractions are quite small. It is not safe positively to assert its smallness, because in such a case the effects of b and K may possibly be run together into a single term, as is done by Callendar in his gas equation for steam at moderate pressures.‡

We will next discuss the reason of the abnormal lowering of vapour pressure in the case of strong solutions. We have seen that—

$$Ps = RT \log \frac{\pi_o}{\pi} \text{ nearly,}$$

or therefore—

$$P = \frac{R_o T}{M_{vap.}\, s} \log \frac{\pi_o}{\pi},$$

where R_o is the value of R per gram molecule.

* Hirn, 1865. Often attributed to van der Waals, whose contribution (1881) consisted in finding a particular value for K and deducing the consequences.

† If K is a function of the temperature this equality no longer holds good.

‡ Hence the difficulty in discriminating between van Laar and Dolezalek and their respective schools.

Let the solution consist of n molecules of solute dissolved in N molecules of solvent, each reckoned as of the same complexity as in the vapour state; let V_w be put equal to $NM_{vap.}S$; and let V be the total volume of the same solution, containing therefore n molecules of solute. Then—

$$P = \frac{nR_oT}{V - nb} = \frac{NR_oT}{V_w} \log \frac{\pi_o}{\pi},$$ *

whence the equation for the lowering becomes—

$$\log \frac{\pi_o}{\pi} = \frac{n}{N} \frac{V_w}{V - nb}.$$

We might at first be tempted to write—

$$V_w = V - nb,$$

in which case Raoult's law would be true for strong solutions (except for the introduction of the logarithm). Experiment shows that this is by no means the case—in fact, V_w is greater than $V - nb$. Let us suppose, as Callendar and others have done, that the molecules of solute become hydrated, each combining with a molecules of solvent. Then if there is no contraction, except what is represented by the difference between s and u for the water, we have—

$$V = nb + (N - na)sM_{vap.}$$

where b represents the volume of a *hydrated* molecule, and therefore includes the volume of a molecules of solvent, and therefore—

$$sM_{vap.} = \frac{V - nb}{N - na},$$

so that $\log \frac{\pi_o}{\pi}$ becomes $= \frac{n}{N - an}$.

This is exactly the formula which Callendar employs. But although the interpretation of a as the hydration factor is the one which he accepts, yet the reason of its entry into this equation would appear to be different from that which he himself gives. In our formula it appears as an effect of alteration of the volume of the solute molecules—each molecule of the hydrated salt being *larger* than that of the unhydrated salt, owing to the water molecules combined with it. On the other hand Callendar, developing ideas which had been foreshadowed by Poynting, interprets the effect of the hydration as being to render ineffective for evaporation a number a of molecules of solvent for each molecule of solute. There is a difficulty in this

* This might also have been obtained from the mathematical identity—

$$\left(\frac{\partial \pi}{\partial n}\right)_p \left(\frac{\partial n}{\partial p}\right)_\pi \left(\frac{\partial p}{\partial \pi}\right)_n = -1$$

taken together with the values—

$$\left(\frac{\partial \pi}{\partial p}\right)_n = \frac{s}{v} = \frac{sM_{vap.}\pi}{R_oT} \quad \left(\frac{\partial p}{\partial n}\right)_\pi = \frac{nR_oT}{V - nb};$$

this gives—

$$-\left(\frac{\partial \pi}{\partial n}\right)_p = \frac{sM_{vap.}\pi}{R_oT} \cdot \left(\frac{\partial p}{\partial n}\right)_\pi,$$

whence by integration—

$$\log \frac{\pi_o}{\pi} = \frac{sM_o n}{V - nb} = \frac{n}{N} \frac{V_w}{V - nb}.$$

In this proof we have taken p and P as practically equal.

latter interpretation which has not yet been pointed out. According to it, $N - an$ is the number of *free* molecules of solvent present in the liquid. But we have seen that N is not the total number in the liquid (even including those combined with the solvent) but the number that would be in the same mass of *vapour* formed from the liquid. Now there is fairly strong evidence that water contains a large number of associated molecules (i.e. molecules combined with each other, $2H_2O$, $3H_2O$, etc.),* so that the real number of liquid molecules in the absence of the solute would not be N but (say) βN. If then we imagine each of the n molecules of solute to render inactive any number a of these, the number of active molecules would be $\beta N - an$, not $N - an$. The theory evidently breaks down in fact, for the form in which it is usually stated even for infinitely dilute solutions, unless we give up the supposition that water (liquid) is associated. It is possible that by some inconsiderable change in the statement of this theory the difficulty might be removed; but the change has not yet been suggested.

The explanation given above of the term an makes it proportional to the increase in the effective volume of the molecules of the solute due to hydration. When this effective volume is calculated (from osmotic pressures or lowering of vapour pressures or any other phenomena into which it enters in the same way) it comes out bigger than the volume expected from the density and molecular weight of solid sugar; and this may be explained by the hydration of the solute, the size of the molecules being thereby increased. The value for the hydration comes out the same as on Callendar's theory, but the underlying conception is totally different.

Addendum.

The following alternative way of finding H_i is very simple.

For any homogeneous fluid we may write: Increase of internal energy—

$$= dE = S dT + T\left(\frac{\partial p}{\partial T}\right)_v dV - p dV,$$

$$= S dT + T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right) dV.$$

When we have two phases at different pressures p and p_0 and volumes V and V_0 we may similarly write—

$$dE = S dT + T^2 \frac{\partial}{\partial T}\left(\frac{p}{T}\right) dV + T^2 \frac{\partial}{\partial T}\left(\frac{p_0}{T}\right) dV_0,$$

where E and S are the energy and the thermal capacity of the double system.

Now in an isothermal change in which $dV = s$ and $dV_0 = -u$, the value of dE is what we have called H_i, i.e.—

$$H_i = T^2\left[s \frac{\partial}{\partial T}\left(\frac{p}{T}\right) - u \frac{\partial}{\partial T}\left(\frac{p_0}{T}\right)\right],$$

in which we remove the restriction as to constant volume during the differentiation as p and p_0 are independent of the volumes for the changes of volume involved.

* See, for example, "General Discussion on the Constitution of Water," *Trans. Farad. Soc.*, July, 1910, where numerous references are given.

THE VAPOUR PRESSURE OF CONCENTRATED SUGAR SOLUTIONS.

By D. ORSON WOOD, B.Sc., A.R.C.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

The measurement of the vapour pressure of highly concentrated solutions is of considerable importance from the point of view of the theory of solution; for it is only when the strength of the solutions used becomes great that the exact form of the theory can be determined. The depression of vapour pressure is usually deduced from experiments on osmotic pressure or freezing-point, and very few measurements of the vapour pressure itself have been made. This is largely due to the difficulty of taking observations of sufficient exactness to enable the difference between the vapour pressures of the solution and the solvent to be obtained without relatively large errors.

In 1912 Dr. Perman and Mr. T. W. Price read a paper before this Society, in which they gave the results of a large number of experiments made by an air-current method. Their data showed variations in the relative lowering of vapour pressure which were unexpected from theoretical considerations, and, in consequence, Professor A. W. Porter suggested to me that it would be useful to attempt measurements by a different method in order to confirm or modify their conclusions. Preliminary results obtained with a very concentrated sugar solution of unknown strength did not agree with Dr. Perman's values, and the following paper contains an account of further observations made on solutions of saccharose. The measurements are by no means as accurate as one could wish, but they are probably the best which have been obtained so far with highly concentrated solutions.

Method.

After a critical examination of the air-current method it seemed difficult to point to any definite source of error other than that possibly introduced by the use of the perfect gas equation in the calculation of the vapour pressure from the experimental data.* This being the case, it seemed desirable to use a direct method which should give the pressures without the necessity of any such calculations. Moreover, the point of immediate interest was the variation of the Babo constant (i.e. the lowering of the vapour pressure relative to that of the solvent) with temperature, and the direct static method lends itself very easily to the determination of the vapour pressure at different temperatures.

The more serious objections usually brought forward against the method are †:—

(*a*) That with so small a quantity of vapour any impurity would produce a large error.

* See also a letter in *Nature* (March 11, 1915) from Lord Berkeley.

† See, for example, Lincoln and Klein, *Jour. Phys. Chem.*, 11, 1907.

(*b*) That, since evaporation takes place from the upper layers only, they become too concentrated and the measured vapour pressure is too small.

With regard to (*a*) the most serious impurity is dissolved air. The removal of this air under the condition that the concentration of the solution must be known constitutes the main difficulty of the experiment. The method used for removing the air would, however, also remove any traces of other volatile substances, should they ever be present. As for (*b*), even at the highest temperatures only a small quantity of vapour is involved, and by stirring the solution magnetically the objection is sufficiently overcome.

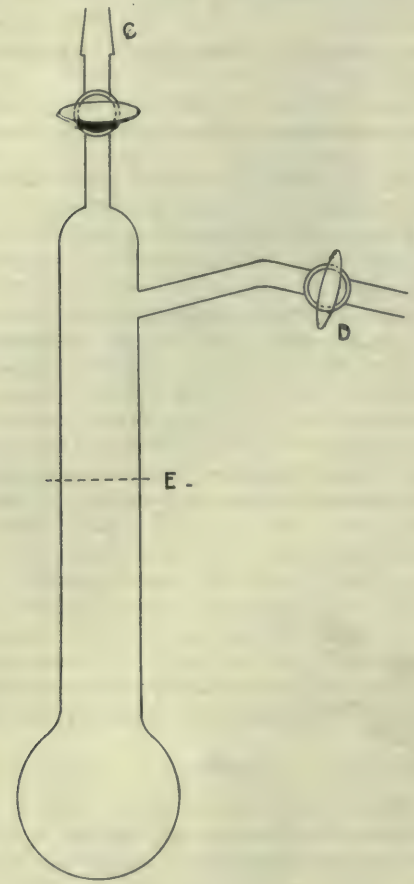


FIG. 1.

Apart from these possible sources of error there is the disadvantage that the preparation of the apparatus for each solution is somewhat laborious, so that the method does not lend itself easily to making experiments with many different solutions.

It is necessary to introduce an air-free solution of known concentration into a vessel in which its vapour pressure can be measured barometrically. After many trials the arrangements shown in Figs. 1 and 2 were adopted. The solution was prepared in the vessel depicted in Fig. 1, and from this vessel it was transferred to the main apparatus (Fig. 2), where its vapour

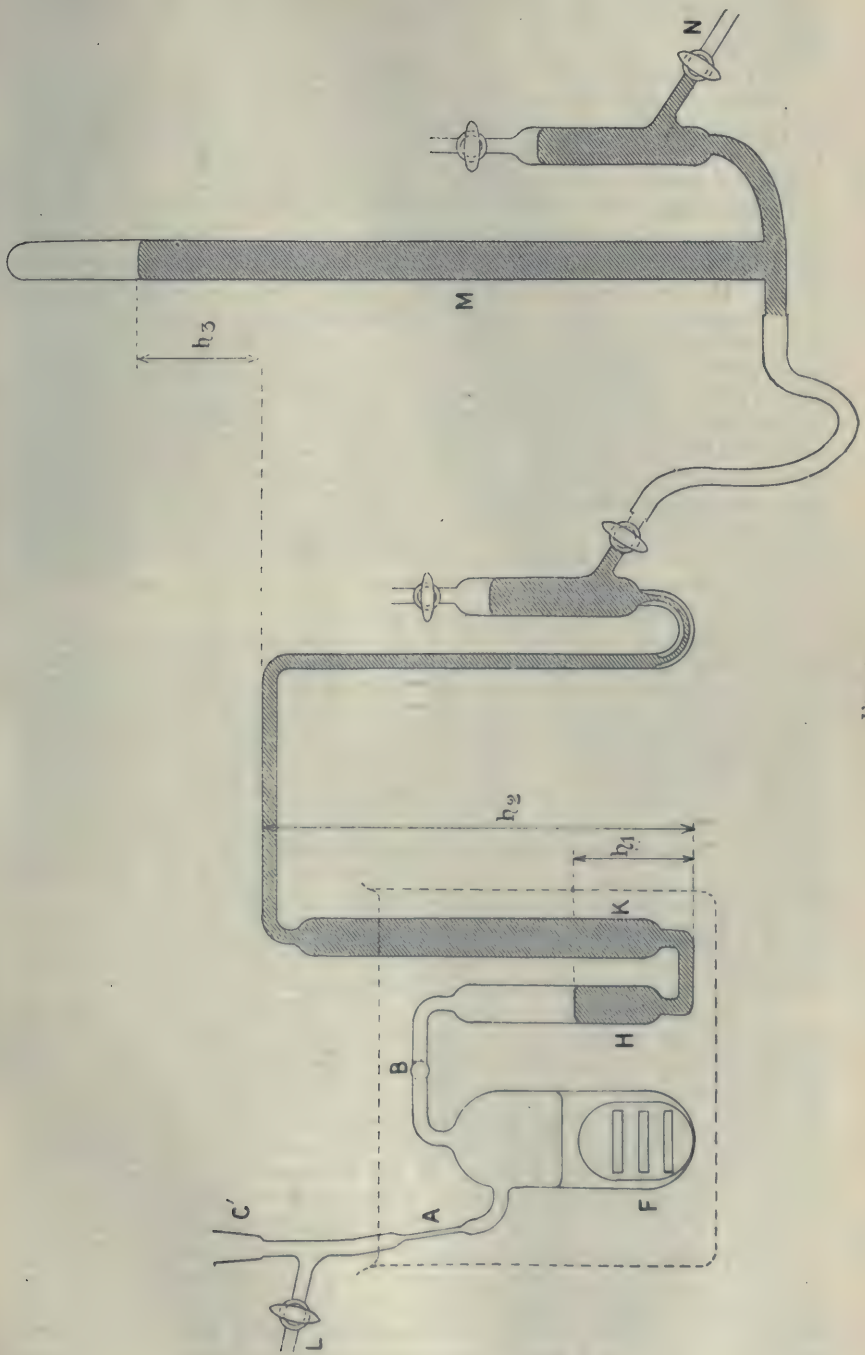


FIG. 2.

pressure was measured. The part of this latter to the left of the constriction A is required only during the filling process, and when that is completed it is sealed off.

The Preparation of the Solution.—The filler consists of a glass bulb blown at the end of a piece of wide glass tubing, about 10 inches long, which serves as a condenser. The tubes C and D are fused to the end of this condenser—C having at its upper end the inner portion of the ground-glass joint through which the filler is ultimately joined to the main apparatus at C′ (Fig. 2). In the preparation of a solution the condenser tube was first cut in two at E, and the two parts thoroughly cleaned with chromic acid. The acid was rinsed out with water, then ammonia, and finally this was removed with distilled water. The two parts were next dried in a hot-air oven, and were then ready for the solution. A quantity of clear saccharose crystals were picked by hand from the main stock and a known mass of them placed in the bulb, which was then fused to the upper part of the filler again. The air was removed with a pump and the vessel and its contents weighed on a chemical balance. In the meanwhile ordinary distilled water was thoroughly boiled in a tube similar to that shown in Fig. 1, except that the branch D was absent. After it had cooled this vessel was inverted and connected to the filler with a short piece of pressure-tubing attached to the end of C. The taps being opened, the requisite amount of "air-free" water was allowed to enter the filler. In this way there was obtained a solution, at least 3 per cent. more dilute than that ultimately required, and containing a minimum of air to be removed in subsequent operations.

The bulb was next connected, at D, through suitable drying tubes, to the air pump, and was carefully warmed. The taps C and D were shielded as far as possible from the direct heat with wet blotting-paper. The whole apparatus being exhausted of air, evaporation was continued until the desired concentration was almost reached. Finally, to remove all traces of air the solution was heated to about 100° C. with the tap D closed. After cooling a little, D was opened, and the air which had been evolved was pumped out. This process was repeated several times. The bulb was then allowed to cool and was weighed. The mass of the bulb, together with a known mass of crystals, having been determined previously, the mass of the water, and, therefore, the strength of the solution, could be calculated.

The operations just described needed the utmost care in the manipulation both of the flame and the air pump, in order that the tendency of the solution to boil by bumping might be kept within reasonable limits.

The Filling Process.—Referring to Fig. 2, the apparatus consists of a bulb F, into which the solution is to be placed, and the arrangement to the right of F, by which the pressure is measured. The wide glass tube H contains the mercury whose meniscus is in contact with the vapour ; close to it is a similar tube K, which is just long enough to project over the top of the water bath in which F, H and K are immersed. This tube is connected, through an air trap, by flexible rubber tubing to the barometer M. The level of the mercury through the whole system is controlled by a mercury reservoir attached to N. The vapour pressure is sufficient to make the mercury column continuous, and the difference in the level of the mercury at H and M gives the required vapour pressure (subject to a small temperature correction to be discussed later). During the measurements the solution in F is stirred by means of a sealed glass tube containing short rods of soft iron embedded in glass wool. These iron rods are dragged up and down by a circular electromagnet just outside the bulb.

In the process of cleaning and filling, F, H, K, and the other rigid parts of

the apparatus were firmly fixed to a wooden frame to which the filler tube, sealed on to the rest by the ground joint CC′, was also attached. The apparatus was completely exhausted of air through the tube L, and the mercury was allowed to flow into H K from N, thus preventing access of vapour to the more remote portions of the apparatus. The tap in C was then opened and the solution, driven by gravity and its own vapour pressure, flowed down slowly into F. When sufficient solution had entered the bulb it was sealed off at the constriction A. This was always one of the critical stages in the experiment; but success was rendered quite certain by softening the constriction with a luminous flame before the apparatus was exhausted. This removed any stress that might have been imposed by the attachment of the comparatively heavy filler bulb, and by the subsequent clamping down on to the supporting frame.

In the earlier experiments, as a final precaution, a tube was sealed on at B in a plane perpendicular to that of the rest of the apparatus. This tube was connected to the pump, and the solution was warmed and stirred in F to remove any residual traces of air, the water vapour evolved being condensed in a bulb surrounded by a freezing mixture. This water was afterwards distilled back into F; but a little was inevitably drawn into the drying tubes, and the uncertainty thereby introduced into the concentration was considered to overbalance any advantage gained by the possible removal of last traces of air, of whose presence, moreover, there was never any certain evidence.

The Measurements.

When the tube F had been filled and sealed up successfully, the apparatus was removed from its supporting frame, and was held by an iron clamp so that the tubes A, H and K were immersed in a water bath. This consisted of a large copper tank with a plate-glass window, through which the level of the mercury in the tube H could be observed. The bath was heated by two independent gas-burners, one arranged so that its flame could be adjusted very finely in order to keep the temperature constant. The stirring was carried out most efficiently by a single propellor fixed in a corner of the tank and driven at a high speed by an electric motor.

A metre scale was set up in a vertical plane midway between H and M, and the divisions on this scale corresponding to the two mercury levels were read off with two cathetometers used as reading telescopes. The reservoir attached to N was manipulated each time so as to bring the mercury meniscus to about the same level in H.

The temperatures were determined with a limited-range thermometer (50° C.–105° C.), divided into tenths and read with a small magnifying lens. The thermometer was afterwards standardized by direct comparison with another limited-range thermometer whose errors were known. Three other thermometers were necessary, (i) to determine the average temperature of the emergent stem, (ii) to measure the temperature in the region between K and M (the thermometer was suspended between the limbs of the U-tube of the air trap), (iii) to measure the temperature of the barometer tube M. A screen was set up to protect the mercury columns outside the bath from direct exposure to heat.

The readings were, at first, corrected for the curvature of the meniscus in H and in M, but as the correction is at the very extreme limit of the possible accuracy and is made very uncertain by the high temperature of the mercury in the tube H, it was afterwards omitted altogether. A small correction is, however, necessary to allow for the difference of temperature of the mercury

columns connecting F and M. This correction in no case exceeded ·12 cm. of mercury, as may be seen from the following considerations :—

The true vapour pressure of the solution is given by the expression $h_3\rho_2 + h_2\rho_1' - h_1\rho_1$, while that actually measured is $(h_3 + h_2 - h_1)\rho_2$, where—

ρ_1 = density of mercury at temperature of bath,
ρ_2 = density at temperature of barometer tubes,
ρ_1 = mean density of column h_2,

and the heights h_1, h_2, and h_3 are marked in Fig. 2. The actual measurement is, therefore, too great by an amount $h_2(\rho_2 - \rho') - h_1(\rho_2 - \rho_1)$, which can be written $\frac{\rho_2 - \rho_1}{\rho_0}(h_2 - h_1)$ in cm. of mercury at 0° C. with sufficient accuracy for these experiments. The exact value of this correction in one experiment is shown in Table I. It could have been eliminated altogether by arranging a second apparatus similar to the first alongside of it, but containing water instead of the solution.

Readings (several at each temperature) were taken with both rising and falling temperatures and on different days—on one occasion spread over as much as three weeks. No consistent differences developed, as would be expected if the sugar began to invert. The results recorded in this paper range from 60° C. to 90° C. ; but readings were obtained at lower temperatures right down to — 10° C. The vapour pressure is then insufficient to support the whole length of the mercury column in the tube K, and the pressure was read off from the difference in level of the surfaces in H and K. The values so determined lay excellently on the vapour pressure curve, but the depression at such low temperatures (i.e. below 60° C.) is so small that the proportionate errors made the observations worthless from the theoretical point of view. The readings at 0° C. and below did, however, show that no appreciable amount of air was present in F at these temperatures, though, of course, it might be evolved reversibly as the temperature rose.

Results.

In order to determine the probable degree of accuracy that would be obtained from the method, an experiment was made with water instead of a solution. The results are given at some length in Table I, so that the magnitude of the various corrections involved may be exhibited.

Table I.

The Vapour Pressure of Pure Water.

Thermometer Reading. °C.	Emergent Stem Correction. °C.	Temperature corrected for Stem and Thermometer °C.	Observed Pressure. cm.	Pressure reduced to cm. Mercury at 0°C.	Pressure corrected for Columns. cm.
58·49	0·00	58·49	13·93	13·89	13·84
62·37	0·02	62·35	16·69	16·63	16·58
65·21	0·03	65·19	18·99	18·93	18·87
68·70	0·05	68·68	22·10	22·02	21·96
72·14	0·06	72·13	25·63	25·54	25·47
77·27	0·11	77·32	31·89	31·77	31·70
80·00	0·15	80·14	35·76	35·64	35·56
84·66	0·20	84·91	43·15	42·99	42· 1
88·85	0·22	89·04	50·63	50·45	50·36

These results were plotted on a large scale, and a smooth curve was drawn through the points. This curve is parallel to, but a little to the right of, that obtained by plotting the standard values of the vapour pressure. The vapour pressure for each 5° above 60° C. was read off from the experimental curve, and the numbers so obtained are shown in Table II.

TABLE II.

The Vapour Pressure of Water.

Temperature. °C.	Value from Curve.	Regnault.	Landolt and Börnstein's Tables.	Difference. cm.	Difference. °C.
60	14·86	14·88	14·92	0·06	0·07
65	18·69	18·71	18·75	0·06	0·07
70	23·28	23·31	23·38	0·10	0·10
75	28·75	28·88	28·93	0·18	0·15
80	35·38	35·46	35·55	0·17	0·12
85	43·10	43·32	43·38	0·28	0·16
90	52·30	52·55	52·60	0·30	0·15

The values given by the experiment are all too small, so that there is no evidence of the presence of dissolved air. The difference is possibly due to impurity in the water used, and, in this connection, it must be pointed out that, during the filling process, the water may become contaminated with grease. No traces of this, however, were ever visible in the solutions, and it does not necessarily follow that the grease would decrease the vapour pressure ; its effect might go the other way. The degree of accuracy shown in these results—rather better than one part in two hundred—is sufficient for most of the purposes of this paper, the more especially as it indicates that the observed pressures are probably too low.

Experiments were carried out with three solutions, referred to hereafter as I, II, and III. They contained approximately 48, 61, and 69 grams of saccharose to 100 grams of solution. Their exact concentrations expressed in the different units in common use are shown in Table III.

TABLE III.

The Concentration of the Solutions.

Solution No.	Grams of Sugar per 100 grams of Solution.	Grams of Sugar per litre of Solution at 20° C.	Grams of Sugar per 100 grams of Water.	$\frac{n}{N} = \frac{\text{Gram molecules of Sugar}}{\text{Gram molecules of Water}}$
I	47·97	585	92·0	·0486
II	61·02	789	156·6	·0824
III	69·20	928	224·3	·1182

The first successful experiment was made with the 69 per cent. solution. In this experiment only hand stirring of the water bath was possible, while, in every other case, a mechanical stirrer was used. In consequence, the

temperatures read in this experiment are only given here to the nearest tenth of a degree. In order to check the concentration, and, in particular, to see that it had not increased owing to evaporation during the filling process, the density of the solution was determined at the end of the experiment. According to this determination the concentration was 69·8 per cent. instead of 69·2 per cent.; as good an agreement as could be expected, and, as the density method was only regarded as a check on the other, the strength calculated from the masses of the sugar and solution at the commencement of the experiment was taken to be correct. It is important to notice that this concentration, if in error at all, will be too small.

The measurements of the vapour pressures of solution I were evidently less satisfactory than the others, because the points, when plotted, did not lie well on the curve drawn through them. In consequence less stress can be laid on the depression of vapour pressure calculated from these results than in the other cases.

TABLE IV.

Solution I.			Solution II.			Solution III.		
T° C.	π_π.	$\frac{\pi_0 - \pi_\pi}{\pi_0}$.	T° C.	π_π.	$\frac{\pi_0 - \pi_\pi}{\pi_0}$.	T° C.	π_π.	$\frac{\pi_0 - \pi_\pi}{\pi_0}$.
60·42	14·60	·041	62·98	15·18	·112	59·0	11·27	·208
63·39	16·58	·048	67·51	18·69	·108	62·9	13·60	·203
66·02	18·47	·057	73·08	23·75	·109	68·2	17·37	·196
72·95	24·78	·065	78·55	29·86	·106	73·9	22·25	·194
74·23	26·25	·062	83·35	36·38	·104	75·1	23·50	·191
80·42	34·49	·045	87·61	42·93	·106	78·8	27·68	·183
82·78	37·39	·058	90·85	48·58	·107	84·9	35·94	·169
84·86	40·10	·070	[92·66	52·71	·093]	89·1	41·64	·181
90·00	49·60	·057				92·0	46·44	·181

π_0 = vapour pressure of water under its own vapour pressure, taken from Landolt.

π_π = vapour pressure of solution under its own vapour pressure.

Table IV gives the result of the observations. Each vapour pressure given in that table is the mean of a number of observations (varying from three to eight) taken at approximately the same temperature, i.e. within 0·5° C. These observations were plotted on a very large scale, and a curve was drawn through the points. In calculating the mean the observations falling much off this curve were given half the weight of the others. The lowering of vapour pressure relative to the vapour pressure of water is shown also, but the values on which the following discussion is based were obtained from large-scale curves plotted from the data given in this table. It will be seen at once that the variation of Babo's constant with temperature is quite small even for such syrupy solutions as are being dealt with here.

Discussion of Results.

The value of the measurements can best be gauged by using them to calculate the heat of dilution of the solutions, and this, therefore, is given first; subsequently they are discussed from the point of view of the theory of solution and of osmotic pressure.

The latent heat of dilution is the heat that must be added to a (theoretically) infinite amount of solution in order to keep its temperature constant when one gram of the solvent is added to it. Defined in this way it is positive when adiabatic dilution is accompanied by cooling.

It will be sufficient for the present argument to assume the well-known Kirchhoff equation, which gives for the latent heat—

$$H = RT^2 \frac{\partial}{\partial T}\left(\log_e \frac{\pi_o}{\pi_\pi}\right)$$

where R, the gas constant for water vapour, varies inversely as the molecular weight of the vapour. It follows, then, that, leaving out of consideration any possible change R may undergo with rise of temperature, the smaller H may be the less should be the variation of $\log \frac{\pi_o}{\pi_\pi}$. Moreover, if H is positive, this expression should increase with rise of temperature, and if H is negative, so that the solution warms when diluted adiabatically, it should decrease. Table V shows the values of the logarithm of the ratio for each solution at different temperatures.

TABLE V.

Temperature. °C.	$\text{Log}_{10}(\pi_o/\pi_\pi)$		
	I.	II.	III.
60	·0212	·0536	·0993
65	·0221	·0508	·0963
70	·0223	·0492	·0944
75	·0236	·0504	·0920
80	·0229	·0496	·0856
85	·0258	·0487	·0827
90	·0252	·0480	·0843

It will be seen that for solutions II and III there is a continuous decrease, while the weakest solution shows an increase with increase of temperature. There do not seem to be many data on latent heats of dilution available. Stackelberg* has measured it in a number of cases, but the strongest solution he used contained about 37 grams of sugar per 100 grams of water; for this he found the latent heat to be —0·31 calories per gram at room temperature, while approximately the same value can be calculated from observations by Morse and his collaborators† of the temperature variation of the osmotic pressure of a solution of about the same strength. (See the section of this paper dealing with osmotic pressure.) The sign of these results corresponds to a decrease in $\log \frac{\pi_o}{\pi_\pi}$ with rise of temperature. A rough experiment‡ with a strong solution at 20° C. gave a much larger negative value

* *Z. für Phys. Chem.*, 26, 1808.

† Moore, Holland, Myers, Cash, and Zinn, *Amer. Chem. Jour.*, 48, 29.

‡ A solution containing 68·6 grams of sugar to 100 grams of solution was prepared. Its specific heat was found to be 0·614. When 87 grams of it were diluted to 63·6 grams sugar per 100 grams solution by adding 6·8 grams of water the temperature *rose* 0·20° C., representing a true rise of 0·18° C. when radiation was allowed for. This gives H of the order — 2 calories per gram at 20° C.

for H, so that it is probable that the ratio should decrease for all three solutions.

The actual value of the heat of dilution at 60° C. (not 20° C.) calculated from the vapour pressure measurements by means of Kirchhoff's equation is — 5·26 cal./gm. for solution II and — 14·03 cal./gm.* for solution III. These values are very large, much larger than the 2 cal./gm. obtained by experiment for solutions of about the same strength, so that the variation of $\log \frac{\pi_o}{\pi_\pi}$ shown by direct measurement is almost certainly too great.

If $\log \frac{\pi_o}{\pi_\pi}$ is plotted against temperature the majority of the points appear to lie on a straight line. If this be correct $\frac{\partial}{\partial T}\left(\log \frac{\pi_o}{\pi_\pi}\right)$ is constant, and the latent heat of dilution should be proportional to the square of the absolute temperature within the limits to which Kirchhoff's equation applies. Magie† has made experiments on several solutes over a range from 3° C. to 27° C., which verify a linear formula due to Thomsen. A calorimeter has been constructed with which it is hoped that measurements may be made over a large range of temperature, so that accurate values of the dilution heat and its variation may be available to test the vapour pressure results.

The measurements made by Perman and Price ‡ at 70° C. and 90° C. with several concentrations, show in every case an increase of $\log_{10} \frac{\pi_o}{\pi_\pi}$ with rise of temperature. Thus, for a solution containing 9·2 gram molecules of saccharose to 100 gram molecules of water, their data give for this expression ·040 at 70° C. and ·056 at 90° C., an increase of 30 per cent., the corresponding value of the latent heat of dilution which can be calculated from this being + 25 cal./gm. This means that, according to their observations, there should be a considerable *cooling* instead of warming when the solution is diluted with water under adiabatic conditions. On the other hand, experimenting with calcium chloride they obtained a small decrease in the ratio with rise of temperature. (E.g. a solution containing 12 gram molecules of salt per 100 of water gave $\log_{10} \frac{\pi_o}{\pi_\pi} = ·384$ at 70° C. and ·358 at 90° C.—a decrease of 6·5 per cent.) This again gives a dilution heat of the wrong sign.§ These figures are sufficient to show that results calculated from air current data are subject to errors which become of serious consequence when the depression of the vapour pressure is required.

Von Babo's Law and the Theory of Solution.—Babo showed that, for dilute solutions, the lowering of the vapour pressure relative to that of the solvent $\left(\frac{\pi_o - \pi_\pi}{\pi_o}\right)$ was independent of the temperature for the same solution, and theory (e.g. Kirchhoff's equation) has since proved that this will only be true

* Porter (*Trans. Faraday Soc.*, 1915, *supra*) has shown that a more accurate expression is—

$$H = T^2 \frac{\partial}{\partial T}\left\{R \log_e \frac{\pi_o}{\pi_\pi} - \frac{c(\pi_o - \pi)}{T}\right\}$$

where c is the "coaggregation factor" in Callendar's gas equation. This equation gives H = − 5·52 cal./gm. for solution II and = − 14·7 cal./gm. for solution III at 60° C. The second term being about 5 per cent. of the first, which is, of course, Kirchhoff's expression.

† *Phys. Rev.*, 35, 1912.

‡ *Trans. Faraday Soc.*, viii.

§ See, for example, Stackelburg, loc. cit.

when the latent heat of dilution is zero. The values of this ratio calculated from the present observations are shown in Tables IV and VI, and while the variation is far smaller than that obtained by Perman and Price, yet, as the calculation of the latent heat of dilution shows, it is seemingly still too large.

It is usual to calculate the molecular weight of the solute in solution from the expression

$$M = \frac{\pi_\pi}{\pi_o - \pi_\pi} \times \frac{18w}{W}$$

where w grams of solute are dissolved in W grams of solvent. If this is applied to the present case, the values of M obtained for solutions I, II, and III at 75° C. are 303, 230, and 175 respectively, thus decreasing with increase of concentration, and for II and III increasing with rise of temperature. Inasmuch as this equation is based on the simple form of Raoult's law (that

$$\frac{\pi_o - \pi_\pi}{\pi_o} = \frac{n}{N + n},$$

where n gram molecules of solute are dissolved in N of solvent), which most certainly is not true here, the calculation has no real meaning.

Callendar * has elaborated the vapour pressure theory due to Poynting, and, according to his view, when the heat of dilution is small, as it is, at any rate, with moderately strong sugar solutions—

$$\pi_\pi = \frac{N - an}{N - an + n}\,\pi_o,$$

where a is a hydration factor representing the number of solvent molecules associated with each molecule of solute. From experiments on the osmotic pressure of sugar solutions at room temperatures and also on the lowering of freezing-point, with solutions of concentration up to 7 molecules of sugar to 100 of water, Callendar found that $a = 5$; though the value showed signs of falling off with the greatest concentration. The values of a calculated from my values of the vapour pressure π_π are shown in Table VI (p. 12).

It will be seen that a does not vary greatly either with concentration or temperature, but is decidedly less than 5. In fact, the mean value for solution II is 3·97 and for III 4·13, that is, 4 in each case, within the limits of experimental error. The calculations are based on values of π_o taken from Kaye and Laby's tables. If my values are used instead, a is less, but does not undergo any important alteration. It seemed best to use the standard values of π_o, since the cause of mine being too low is uncertain. The values of π_π required to make $a = 5$ have been calculated in each case, and, as will be seen from the table, they are much smaller than those observed. They are quite out of the range of the experimental error indicated by the experiment with pure water, which gave values too low and not too high, as these would need to be to make a greater. Assuming, however, that the difference is due to experimental error, it might arise in two ways :—

(i) Air not sufficiently removed from the solution. No less care was taken to remove the air from the solutions than with the water; moreover, it is suggestive that the supposed error in π_π increases with rise of concentration (at 90° C. the difference is 0·20, 0·91, and 3·21 for solutions I, II, and III respectively) and does not vary in a random fashion, as might be expected, from a fortuitous quantity of residual air. As a matter of fact it was feared that experiment II might fail owing to leakage through the glass of the filler tube, which had devitrified with frequent fusing at the cut E (Fig. 1).

* *Proc. Roy. Soc.*, A, 90, 1908.

TABLE VI.

Temp.	π_o.	π_π.	$\pi_o - \pi_\pi$.	$\frac{\pi_o - \pi_\pi}{\pi_o}$.	a.	π_π (calc.) $a = 5$.	$\pi_\pi - \pi_\pi$ $a = 5$.
	Solution II. $\frac{n}{N} = \cdot0824$.						
60°	14·92	13·19	1·73	·116	4·51	13·09	0·10
65°	18·75	16·68	2·07	·110	4·04	16·44	0·24
70°	23·34	20·84	2·50	·107	3·78	20·46	0·38
75°	28·92	25·75	3·17	·110	4·04	25·37	0·38
80°	35·52	31·68	3·84	·108	3·85	31·17	0·51
85°	43·31	38·72	4·59	·106	3·69	37·99	0·73
90°	52·55	47·06	5·49	·105	3·60	46·15	0·91
	Solution III. $\frac{n}{N} = \cdot1182$.						
60°	14·92	11·87	3·05	·204	4·56	11·58	0·29
65°	18·75	15·02	3·73	·199	4·43	14·53	0·49
70°	23·34	18·79	4·55	·195	4·33	18·09	0·70
75°	28·92	23·40	5·52	·191	4·22	22·40	1·00
80°	35·52	29·16	6·36	·179	3·87	27·54	1·62
85°	43·31	35·80	7·51	·174	3·71	33·60	2·20
90°	52·55	43·28	9·27	·176	3·78	40·07	3·21

(ii) Concentrations incorrect. Taking the average values of $\frac{\pi_o - \pi_\pi}{\pi_o}$, a would become 5 if the concentrations $\left(\frac{n}{N}\right)$ were ·0435, ·0758, and ·1073 instead of ·0486, ·0824, and ·1182 respectively. Thus the solutions would need to be weaker than they were estimated to be, while in reality, as has been pointed out already, the calculated value must be, if anything, too small. The differences, then, are real, and it remains to inquire what may be taking place in the solution in order to account for them.

The relation from which a is calculated is only intended to apply when the latent heat of dilution is small. This may be seen at once by writing it in the form

$$a = \frac{N + n}{n} - \frac{1}{\frac{\pi_o - \pi_\pi}{\pi_o}}.$$

For a solution of given strength $\frac{N + n}{n}$ is constant. Therefore the constancy of a would imply the constancy of $\frac{\pi_o - \pi_\pi}{\pi_o}$, which is an approximate form of $\log_\epsilon \frac{\pi_o}{\pi_\pi}$, and this, according to Kirchhoff, is constant only when H, the dilution heat, is zero. If H is not zero the relation may perhaps still be used by writing n' for n, where n' represents the *effective* number of sugar molecules present in N of water, calculated so as to keep a constant.* This change is equivalent to that made to allow for the ionization of electrolytes, and, since

* Callendar, loc. cit.

the heat of dilution is generally connected with association or dissociation of molecules, the alteration is not unreasonable.

The values of n', assuming $a = 5$, are shown in Table VII below for solution III, for which n is 11·82 molecules per 100 of water.

TABLE VII.

Temperature.	60°.	70°.	80°.	90°.
n'	11·23	10·95	10·43	10·33

It will be seen that the effective number of solute molecules calculated in this way decreases as the temperature rises; thus implying *association* of the *solute increasing* with *rise of temperature.* This result will always be obtained when the latent heat of dilution is negative, for then $\frac{\pi_0 - \pi_\pi}{\pi_0}$ must decrease with rise of temperature, consequently so must $\frac{n'}{N - (a-1)n'}$, or $\frac{n'}{N - 4n'}$ in the present case when a is constant and $= 5$. This requires that n' itself should diminish, N, of course, being constant. It seemed, at first sight, as if this result was contrary to the laws of thermodynamics; but such is not the case. The van 't Hoff isochor leads to the well-known statement that "rise of temperature favours the system formed with absorption of heat." Therefore, an association which increases with rise of temperature must be endothermic; now, dilution at constant temperature causes the associated molecules to dissociate again, since for weak solutions $n' = n$, i.e. it produces an exothermic reaction, so that the latent heat of dilution is negative.

If this association does not occur, then the only alternative is to suppose that lower hydrates are formed, and that there are present in a given solution, at a given temperature, definite proportions of two or more different hydrates. The observations are neither sufficiently numerous nor sufficiently accurate to indicate the law governing the variation of this hydration with concentration; only the change is probably very small.

Thus far the discussion has been limited to the variation of vapour pressure with temperature at constant mass concentration. There is very little to be said about the variation of pressure with concentration. Fig. 3 is drawn to show the manner in which the ratio $\frac{\pi_\pi - \pi_0}{\pi_0}$ varies at 70° and 90° C. The diagram shows (*a*) Perman and Price's measurements, (*b*) the results recorded in this paper, and (*c*) curves calculated from Callendar's formula by putting $a = 4$ and 5. It will be seen that Perman's values lie on straight lines, specially those at 90° C.—implying that Wüllner's law is obeyed—but some little adjustment would be necessary to make the points pass through the origin. The experimental values appear to correspond well with Callendar's curve when $a = 4$ not 5, but it must be remembered that the curves obtained by giving a successive integral values are quite close together, and this is more particularly the case when $\frac{n}{N}$ is small; thus my two points at 70° and 90° C. for $\frac{n}{N} = 0486$ correspond to $a = 1{\cdot}66$ and $a = 3{\cdot}97$ respectively.

According to Perman's observations the vapour pressure is inversely proportional to the concentration $\left(\frac{n}{N}\right)$, while my measurements indicate that it decreases more rapidly than this.

The Osmotic Pressure.—It is not to be expected that accurate values of the

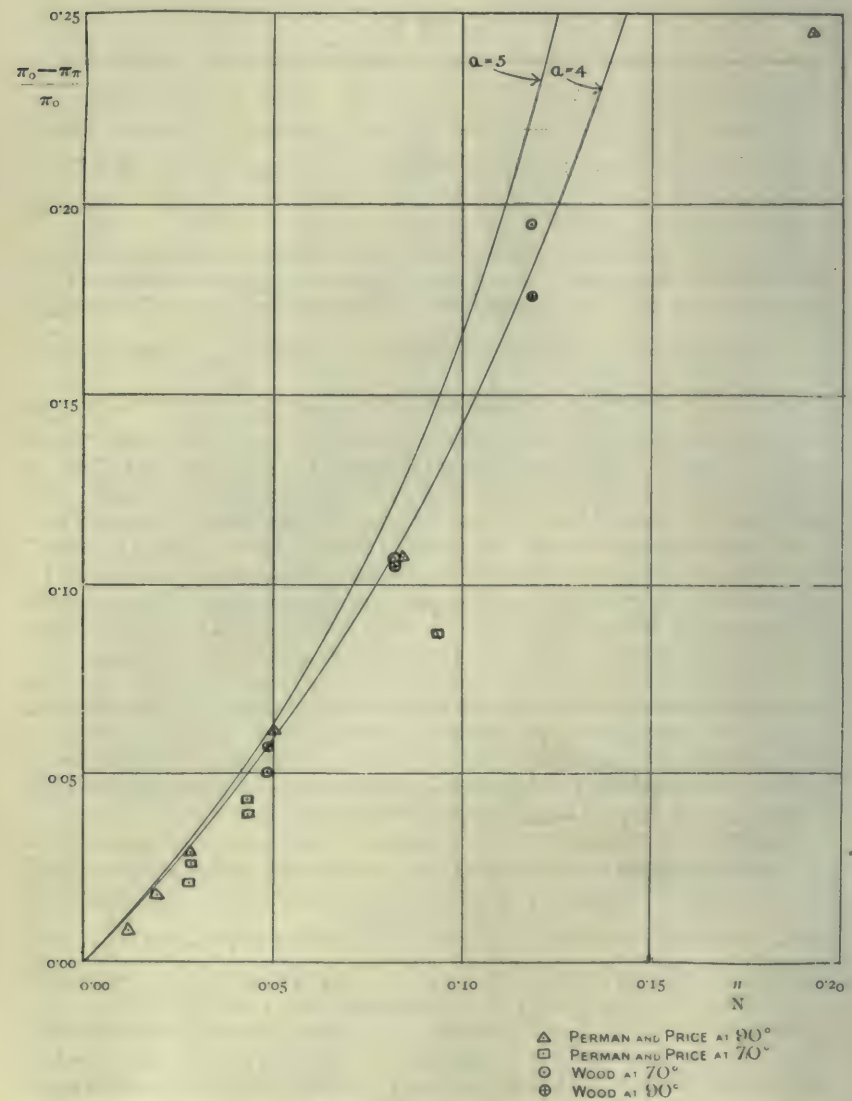


FIG. 3.

osmotic pressure can be deduced from vapour pressure observations, since the calculation requires, in effect, an accurate knowledge of the depression $\pi_0 - \pi_\pi$ and therefore any error in π_π has a considerable influence on the final result. Nevertheless, since no experimental values have been obtained with solutions approaching the concentrations used here, or at the temperatures of these experiments, it is of some interest to attempt the calculation.

Porter * has developed the exact relation which connects the osmotic pressure and the vapour pressures of the solution and solvent. He gives it in the form—

$$\int_{\pi_\pi}^{p} s\,dp = \int_{\pi_\pi}^{\pi_o} v\,dp + \int_{\pi_o}^{p - P_p} u\,dp$$

where, in addition to the symbols already used—

s = "shrinkage" in the volume of the solution when 1 gram of solvent is removed from an infinite volume.
u = specific volume of the liquid solvent.
v = specific volume of the solvent vapour.
p = hydrostatic pressure on the solution.
P_p = osmotic pressure of solution when it is under the pressure $p = p - \pi_o$ when the solvent is under its own vapour pressure.

To integrate this we will use Callendar's gas equation

$$v = \frac{RT}{p} - c + b,$$

which has been shown to represent the behaviour of water vapour with considerable accuracy. In this equation b is a constant volume of the order u; while c depends on the temperature, being equal to $c_o \left(\frac{T_o}{T}\right)^{3\cdot33}$, and for the temperatures dealt with here is of the order of 30 c.c. To allow for the compressibility of the liquid we write—

$$s = s_o(1 - ap),$$

and in the small correcting term so introduced put a equal to the compressibility of water.

Integrating and rearranging, we have at once—

$$P_p s\left(1 - \frac{a\,P_p}{2}\right) = RT \log_e \frac{\pi_o}{\pi_\pi} - c(\pi_o - \pi_\pi) + (b - s)(\pi_o - \pi_\pi),$$

the term involving u vanishing when the limits are inserted. The suffix in the term P_p will be dropped, it being noted that the osmotic pressure dealt with is that at T° C. when the solvent is under its own vapour pressure. In applying the equation, even to the present case, the first term on the right alone is important, and it is certainly permissible to drop $(b - s)(\pi_o - \pi_\pi)$, since both b and s are nearly equal to 1.

The shrinkage s is by definition equal to $\left(\frac{\partial V}{\partial M}\right)_m$; where V is the total volume of a solution made up of M gram of solvent and m of solute. It can be calculated from this expression; but a form given by Callendar † is more convenient. It is

$$s = v - c\frac{dv}{dc},$$

where v is the specific volume of the solution and c, the concentration, is equal to $\frac{m}{M}$. This requires a knowledge of the density of the solution for different concentrations at each temperature for which P is to be calculated.

* *Proc. Roy. Soc.*, 79, A, 1907. † Loc. cit.

Landolt and Börnstein give results obtained by Plato * up to 60° C., so that as far as this temperature the data for s are known. Above this its value must be found by extrapolation. It was observed that, for a given value of c, $\frac{dv}{dc}$ showed no certain change with temperature from 20° to 60° C., so that s, within this range, was less than v by a certain constant volume. It was assumed that this constant difference was maintained up to 90° C.

As a sample calculation we have for solution I at 60° C.—

$$P\left(1 - \frac{\cdot 000041}{2} P\right) = \frac{8\cdot 315 \times 10^7 \times 333 \times 2\cdot 303 \times \cdot 0212}{18 \times 1\cdot 013 \times 76 \times 981 \times 13\cdot 59} - \frac{38\cdot 68 \times \cdot 71}{1\cdot 013 \times 76}$$
$$= 73\cdot 16 - \cdot 36$$
$$= 72\cdot 8,$$

or—

$$P = 72\cdot 8 + \cdot 0000205 \times 72\cdot 8^2 = 72\cdot 8 + \cdot 1 = 72\cdot 9 \text{ atmos.}$$

The values of P given in Table VIII were calculated in this way. Those in square brackets are deduced from values of $\log \frac{\pi_o}{\pi_\pi}$ taken from a straight line drawn through the points obtained by plotting the ratio against T. The others are calculated from the vapour pressures read off from the curves.

It will be seen that, for II and III, the calculated value of the osmotic pressure has a distinct tendency to diminish with rise of temperature and not to increase; a result sufficiently unexpected to merit a little theoretical consideration apart from the question of the accuracy of the observations on which the calculations are based. It has been firmly established that these sugar solutions warm when they are diluted adiabatically, so that according to Kirchhoff's equation, and quite independently of the results recorded in this paper, $\log_\epsilon \frac{\pi_o}{\pi_\pi}$ would decrease as the temperature rises; while at the same time the c term becomes increasingly negative. If, therefore, the logarithm decreases faster than the temperature increases the osmotic pressure must decrease.

If we were to accept the suggestion that negative heats of dilution imply an association of solute molecules, the amount of which becomes greater at the higher temperatures, then the dynamical explanation would be that the increased association more than balanced the increase of kinetic pressure due to the rise of temperature. On the other hand, if Callendar's hydration factor a changes, owing to the formation of simpler hydrates at the higher temperatures, then one might consider the increase in the effective dilution due to the liberation of the water previously attached to the sugar molecules to be responsible for the decrease in the osmotic pressure.

Some years ago when Berkeley and Hartley first published their measurements of the osmotic pressure of strong sugar solutions, Professor Porter found that their results could be represented fairly well by the equation—

$$P = \frac{nR_oT}{V - nb},$$

where n is the number of sugar molecules in V c.c. of solution and R_o is the universal gas constant. In this expression b will be of the order of the volume of one gram molecule of sugar together with its attached water molecules. Substituting Berkeley and Hartley's values of P we find b to come out approximately equal to 280 c.c.; the values of P, shown in Table VIII,

* Plato, *Abhdl. Norm. Eich.-Komm.*, 2, 140, 1900.

TABLE VIII.

Temperature °C.	Solution I.					Solution II.					Solution III.				
	S.	$\frac{RT}{S}\log_\epsilon\frac{\pi_o}{\pi_\pi}$	$-\frac{C}{S}(\pi_o-\pi_\pi)$	$\frac{aP^2}{2}$	P.	S.	$\frac{RT}{S}\log_\epsilon\frac{\pi_o}{\pi_\pi}$	$-\frac{C}{S}(\pi_o-\pi_\pi)$	$\frac{aP^2}{2}$	P.	S.	$\frac{RT}{S}\log_\epsilon\frac{\pi_o}{\pi_\pi}$	$-\frac{C}{S}(\pi_o-\pi_\pi)$	$\frac{aP^2}{2}$	P.
60	1·013	73·16	−·36	+·11	72·9	1·006	186·4 [183·2]	−·9	+·7 [+·7]	186·2 [183·0]	1·001	346·8	−1·5	+2·4	347·7
70	1·019	78·83 [80·25]	−·52	+·13 [+·13]	78·4 [79·8]	1·013	175·9 [182·9]	−1·2	+·6 [+·7]	175·3 [182·4]	1·008	337·4	−2·1	+2·3	337·6
80	1·026	82·73 [86·35]	−·78	+·14 [+·15]	82·1 [85·7]	1·020	180·3	−1·6	+·6	179·3	1·015	312·6 [326·1]	−2·6	+2·0 [+2·2]	312·0 [325·7]
90	1·032	93·04	−1·05	+·18	92·2	1·025	178·5	−1·9	+·6	177·2	1·020	315·0	−3·5	+2·0	313·5

calculated for solutions of much greater concentration and at considerably higher temperatures (90° instead of 20°) give the same result. This supports the belief that the mean values of the osmotic pressures given in this paper for each solution are reasonably correct even if the variation with temperature is not. It leads also to an interesting check on the calculations ; for example, for solution II at 60° C., $a = 4{\cdot}51$ and b works out to be 283 c.c.* : at 90° C., $a = 3{\cdot}60$ and $b = 265$ c.c. ; thus the volume of the sugar molecule has apparently decreased by 18 c.c. while a has diminished by ·91 molecule or 16·5 c.c.

Differentiating the equation for P with respect to T we obtain—

$$\frac{dP}{dT} = \frac{P}{T}\left(1 + \frac{P}{R_o}\frac{db}{dT}\right)$$

which makes P independent of the temperature when $\frac{db}{dT} = -\frac{R_o}{P}$. This means that when P = 180 atmospheres (as it does for solution II) a loss of 1 molecule of water for each 40° C. rise of temperature would suffice. A greater rate of dehydration than this would involve a decrease of the osmotic pressure with rise of temperature.

It is probable, however, that this stage is not reached in the present case, and that the real osmotic pressure does not diminish in the manner shown in Table VIII, for it will now be shown that the manner in which the calculated values change is due to the too rapid variation in the experimental values of $\log \frac{\pi_o}{\pi_\pi}$ with temperature.

Writing—

$$Ps = RT \log \frac{\pi_o}{\pi_\pi}$$

and assuming R to be independent of temperature, we have—

$$\frac{\partial}{\partial T}\left(Ps\right) = RT\frac{\partial}{\partial T}\left(\log \frac{\pi_o}{\pi_\pi}\right) + R \log \frac{\pi_o}{\pi_\pi}.$$

For Ps to be independent of T, $\frac{\partial (Ps)}{\partial T} = 0$. Substituting for $\frac{\partial}{\partial T}\left(\log_\epsilon \frac{\pi_o}{\pi_\pi}\right)$ from Kirchhoff's equation we then obtain—

$$\frac{H}{T} = -R \log_\epsilon \frac{\pi_o}{\pi_\pi},\dagger$$

a special equation for the latent heat of dilution which holds approximately only when the osmotic pressure is independent of temperature, the change in s being quite small (2 per cent. in 30° C.). For solution II at 60° C. the value of $-RT \log_\epsilon \frac{\pi_o}{\pi_\pi}$ is $-4{\cdot}44$, whereas Kirchhoff's equation applied to the same data gives $H = -5{\cdot}16$, a value which corresponds to a slow diminution of P with rise of temperature. Reasons have been given in the section on

* If b be assumed to be equal to the volume of the hydrated molecule in the solution, then for solution II at 60° C. this volume (283 c.c.) is 68 c.c. greater than that of the sugar molecule alone (215 c.c.). This difference is equal to the volume of 3·8 water molecules instead of 4·5, a good agreement in view of the fact that some shrinkage would be expected to take place.

† On looking through Callendar's paper after this expression had been obtained, it was found that, giving an equation similar to this, he contemplates a possibility of P being independent of, but not diminishing with, T.

latent heat of dilution for supposing that the true value of the latent heat is smaller than this, so that the correct conclusion to be drawn from the calculations is that at higher temperatures with these strong solutions P alters very slowly with temperature.

The latent heat of dilution can be calculated from the osmotic pressure from the following equation due to Porter*—

$$\frac{H}{T^2} = (s - u)\frac{\partial}{\partial T}\left(\frac{\pi_\pi}{T}\right) + u\frac{\partial}{\partial T}\left(\frac{P}{T}\right),$$

where all the symbols have their previous meaning. This formula was applied to calculate H from the results of Morse and his assistants already mentioned; the $(s - u)$ term being neglected. Applied to the present case it gives H at 60° C.—

for solution II = — 5·62 cal./gm.
for solution III = — 15·9 cal./gm.

—values which agree well with those calculated directly from Porter's modification of Kirchhoff's equation.

Summary and Conclusion.

1. A static method suitable for the determination of the vapour pressure of highly concentrated solutions is described.

2. Measurements of the vapour pressures of three sugar solutions, of strength varying from 48 to 69 per cent., are given.

3. These results are shown to lead to values of the latent heat of dilution of the right sign and order.

4. Their bearing on the hydration theory is discussed, and Callendar's hydration factor a is shown to vary regularly through the value 4.

5. The vapour pressures are used to calculate the osmotic pressure, which, while of the right order, is found to have a tendency to diminish with rise of temperature. This result is considered theoretically, and it is concluded that, while it is probable that the real osmotic pressure does not diminish, yet it certainly changes very slowly with temperature in the case of these strong solutions.

In conclusion, I must express my very great gratitude to Professor Porter for his unwearying kindness and attention throughout the whole course of this work.

University College, London,
March, 1915.

Joint Discussion on Papers by Professor A. W. Porter and Mr. D. Orson Wood.

Dr. G. Senter said that Professor Porter had already made contributions of fundamental importance to the thermodynamical treatment of osmotic pressure, and the clear discussion of the accuracy of von Babo's law in his present Paper was obviously also of great value. The only part of the Paper he felt competent to discuss was the last section, dealing with the physical meaning of Kirchhoff's equation. Professor Porter, from entirely different

* *Trans. Faraday Soc.*, 1915, *supra*.

premises, deduces the same formula as that previously obtained by Callendar, in which the deviation from the simple law is ascribed to hydration. In Professor Porter's discussion the effective volume of the solute calculated from osmotic pressure or lowering of vapour pressure comes out larger than the volume expected from the density and molecular weight of solid sugar, and he ascribes this increased volume to hydration, so that the term in question has the same signification as in Callendar's equation. The hydration interpretation, however, does not seem to be proved ; other causes, such as molecular attraction, might have exactly the same effect in bringing about a deviation from the calculated volume. The validity of the hydration hypothesis as the sole determining factor in causing the deviation in question becomes still more doubtful when it is recalled that according to the Callendar formula—which is also Professor Porter's formula—sodium and potassium chlorides are more highly hydrated in aqueous solution at 100° than at 0°, an improbable result from a chemical standpoint.

It is essential that these theoretical considerations should be checked by measurements of vapour pressures in concentrated solution, and from this point of view Mr. Wood's experiments are of the utmost value.

Mr. F. J. Harlow asked whether, in dealing with the connection between osmotic pressure and the vapour pressure of a solution, Professor Porter had taken into consideration the fact that observed values of vapour pressure would correspond to the concentration and osmotic pressure in the surface, which are different from those in the body of the solution on account of adsorption.

Mr. E. H. Rayner : From the Papers and discussion it seems that an accurate determination of the temperature change when a strong solution is diluted would afford valuable information. The change is small, amounting perhaps to 0·2°, and if this amount could be measured to about 1 in 1,000 it would be very useful. The Beckmann thermometer is the usual instrument employed, but it cannot be considered altogether satisfactory. Electrical resistance measurements by Wheatstone bridge arrangements can be made sufficiently sensitive to show a change of 1 part in 2 millions or more in the resistance of one branch. As many metals, such as copper and iron, change in resistance by more than 1 part in 2,000 per degree C., a simple resistance measurement of a coil of wire immersed in the liquid will show a change of 0·001° C. If a Wheatstone bridge be made up with four approximately equal resistances, two opposite ones being manganin and the other two copper, the whole immersed in the liquid, the sensitivity is doubled, with other incidental advantages. Balance is obtained in the galvanometer circuit by shunting one of the high sides of the quadrilateral with a relatively high resistance. The above figures with a galvanometer of good sensitivity and suitable resistance are on the conservative side, so that it might be possible to measure small changes of temperature to a few ten-thousandths of a degree with proper precautions.

Mr. E. P. Perman wrote saying that he had looked through Mr. Orson Wood's Paper with much interest, and he thought it probable that his results were more accurate than those of Mr. Price and himself. He was still working at the subject, and hoped to communicate the results to the Society later on.

Mr. D. Orson Wood thanked Dr. Perman for his remarks, and pointed out the great difficulty of obtaining results with these syrup-like solutions of sufficient accuracy to stand the theoretical tests imposed on them.

Professor Alfred W. Porter (*partly communicated*) : I must thank Dr. Senter for his remarks upon my Paper. I wish further to say that he seems

to overestimate the exclusiveness of my advocacy of the hydration theory of vapour pressures. In the Paper itself I show that, as far as the heat of dilution is concerned, it might, on certain suppositions, be attributed entirely to the work done against intermolecular forces, i.e. $H_i = K_s$, where K is the intrinsic pressure. At the same time I emphasize the impossibility of picking out the separate contributions of K and b in a Hirn formula to the heating effect. My object in the concluding part of my Paper was to show that a perfectly consistent and simple account of the vapour pressure law can be given in terms of the augmentation of the volume of the solute molecule as a result of hydration.

Dr. Senter considers that it leads to an impossible result in the case of potassium chloride, in so much as Callendar has shown that it requires that this salt shall be more hydrated in aqueous solution at 100° C. than at 0° C. It is true that this increased hydration is not what is usually expected on chemical grounds; but I wish to point out that it is in no way inconsistent with thermochemical data. Let us suppose that the thermal changes on dilution are wholly due to increased hydration—a supposition entirely in accordance with the law of mass action. Now the latent heat of dilution of KCl solution is positive; i.e. the hydration of KCl in solution on this supposition is an endothermic change. The necessary consequence is that the amount of hydration will increase with rise of temperature. This is precisely what Callendar finds as an inference from the vapour pressure curves. Thus the supposition made is consistent with all the data involved. [A similar argument is employed by Mr. Wood in connection with the possibility of increased association.] Of course, this agreement does not prove the truth of the special supposition; but it at least shows that the criticism is not sound.

At the same time it must be admitted that there is an indeterminateness about the problem which still requires to be removed. On the basis of the existence of molecular attractions van Laar obtains a vapour pressure formula which for moderate dilutions reduces to the forms which Callendar and myself have given. For a binary mixture of which one component is involatile his formula for the vapour pressure reduces to—

$$\pi = \pi_0(1 - \mu)\epsilon^{-a\mu^2},$$

where $\mu = \frac{n}{N + n}$, i.e. the molar fraction of the non-volatile constituent, or in our case of the solute. Retaining only terms of the second degree in μ, this becomes—

$$\frac{\pi_0 - \pi}{\pi} = \frac{n}{N - (a + 1)n}.$$

It would appear that the rival theories require to be carried much further before it will be possible to discriminate between them. Can it be said that either one theory or the other is more exact than to the first power of n in the denominator? The argument of van Laar is founded so definitely on mechanics that we can with almost complete certainty answer this question in the negative. Callendar's argument is an empirical one, so an answer to the question in his case is more difficult to make. I should certainly not claim greater accuracy than this for the formula I have given in the paper.

In reply to Mr. Harlow, the vapour pressure referred to in thermodynamical considerations is the observed vapour pressure for the concentration (and osmotic pressure) of the main body of the solution at its existing

hydrostatic pressure and temperature. Any surface effects which control these data are automatically allowed for in the equations. Adventitious effects which modify these data require special consideration. For example, electrification of the surface is an adventitious effect, the immediate consequence of which is a difference of hydrostatic pressure on the two sides of the electrification, which of course must be allowed for. No such effect arises from adsorption. There can be no obscurity on such questions if the osmotic pressure be defined directly as the difference of hydrostatic pressure, $p - p_0$, on the two sides of the semi-permeable membrane when equilibrium exists.

ON WILLARD GIBBS' ADSORPTION COEFFICIENT.

By ALFRED W. PORTER, D.Sc., F.R.S.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

The following is put forward as an outline of a proof of Gibbs' adsorption theorem, which is easily extended to the case of strong solutions.

Consider a solution of n molecules of solute in N vapour-molecules* of liquid solvent in contact with vapour. Let the total volume of both liquid and vapour be V and the pressure (which is also the vapour pressure) be π.

In any elementary displacement in which evaporation or change of area of interface takes place we have—

$$dU = Td\phi - \pi dV + \sigma dA$$

and

$$d(U - T\phi + \pi V) = -\phi dT + V d\pi + \sigma dA.$$

Now because each side is a perfect differential—

$$\left(\frac{\partial V}{\partial A}\right)_{\pi} = \left(\frac{\partial \sigma}{\partial \pi}\right)_{A}$$

at constant temperature.

Now—

$$\left(\frac{\partial V}{\partial A}\right)_{\pi} = \left(\frac{\partial V}{\partial N}\frac{\partial N}{\partial A}\right)_{\pi}.$$

In this equation $-\left(\frac{\partial N}{\partial A}\right)_{\pi}$ means the number of solvent molecules that must be allowed to evaporate in order to keep π and therefore the concentration constant when the area of the interface increases by unity. If $-\left(\frac{dn}{dA}\right)_{\pi}$ is the number of solute molecules that have been at the same time transferred to the interfacial layer (in other words, Gibbs' constant) we have, since dN and dn must be in the same proportion as N and n—

$$\left(-\frac{\partial N}{\partial A}\right)_{\pi} = -\frac{N}{n}\left(\frac{\partial n}{\partial A}\right)_{\pi} = +\frac{N}{n}\Gamma.$$

Further, if we may neglect the shrinkage of solution due to the above change $\left(-\frac{\partial V}{\partial N}\right)$ is simply the molecular specific volume v of the vapour and $v = \frac{R_0 T}{\pi}$ approximately.

* i.e. molecules of the liquid estimated as of the same complexity as in the vapour.

So—

$$+\frac{N}{n}\Gamma \cdot \frac{R_oT}{\pi} = \left(\frac{\partial\sigma}{\partial\pi}\right)_A$$

and since $d\pi/\pi = -\frac{dn}{N}$ approximately, we have, finally putting $\frac{n}{N} = C$,

$$\Gamma = -\frac{C}{R_oT}\left(\frac{\partial\sigma}{\partial C}\right)_A.$$

This is the usual equation.

If, on the other hand, we do not wish to neglect the shrinkage s of the solution we must put—

$$\left(-\frac{\partial V}{\partial N}\right) = v - s,$$

and may further put it $= \frac{RT}{\pi} - c$, where c is practically Callendar's c in his gas equation, but measured for a gram-molecule instead of for unit mass.

Again $\left(\frac{\partial N}{\partial A}\right)_\pi$ still equals $\frac{N}{n}\left(\frac{\partial n}{\partial A}\right)_\pi$ exactly, so that—

$$\frac{N}{n}\Gamma(v - s) = \left(\frac{\partial\sigma}{\partial\pi}\right)_A \text{ exactly,}$$

or—

$$\Gamma\frac{N}{n}\left(\frac{R_oT}{\pi} - c\right) = \left(\frac{\partial\sigma}{\partial\pi}\right)_A \text{ approximately.}$$

This is a very accurate, though not an exact equation for solutions at ordinary temperatures. The value of c is very small; neglecting it, the equation can be written—

$$\Gamma = -\frac{(1 - aC)^2C}{R_oT}\left(\frac{\partial\sigma}{\partial C}\right)_A$$

where $C = \frac{n}{N}$ and $\log\frac{\pi_o}{\pi}$ has been taken equal to $\frac{n}{N - an} = \frac{C}{1 - aC}$, where a is the hydration factor.*

This should be a good approximation for even strong solutions. The correcting term aC is then not small. For example, for a strong solution of sugar for which $C = 0{\cdot}118$ and $a = 4$, the value of Γ is only one-quarter of its uncorrected value.

* Porter, *Trans. Faraday Soc.*, 1915, *supra*.

A SIMPLE METHOD OF DERIVING THE GIBBS ADSORPTION FORMULA.

By F. J. HARLOW, B.Sc., A.R.C.S., and R. S. WILLOWS, M.A., D.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

While lecturing on "Surface Tension" to chemistry students, mathematical proofs being kept in the background as far as possible, one of the authors has been struck by the difficulty of referring members of the class to simple proofs of some of the necessary thermo-dynamical formulæ. This is notably so in the case of the Gibbs adsorption formula. The most direct and powerful method of treating such problems is undoubtedly by the use of chemical potential; unfortunately the significance and exact meaning of this function are scarcely ever grasped by students. The following simple method may therefore be found useful by teachers.

Let U be the internal energy of a given mass of solution, whose osmotic pressure is p and volume v; let also σ be the surface tension, S the area of the surface at which adsorption is to be considered, θ the absolute temperature, and ϕ the entropy.

Let S and v be changed by small amounts dS and dv at constant temperature, where dv is an increase in the volume of the solution due to an influx of solvent through a semi-permeable membrane. It may be necessary to supply a quantity of heat dH to fulfil this condition, where $d\mathrm{H} = \theta \,.\, d\phi$.

Then the change in U is given by—

$$d\mathrm{U} = \theta \,.\, d\phi + \sigma \,.\, d\mathrm{S} - p \,.\, dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

since work has to be done *on* the surface to increase its area, and *by* the solution when the volume is increased.

Put—

$$\psi = \mathrm{U} - \theta\phi + pv.$$

Then—

$$d\psi = -\phi \,.\, d\theta + \sigma \,.\, d\mathrm{S} + v \,.\, dp, \quad \text{from (1)} \quad . \quad . \quad . \quad (2)$$

or, since the temperature is constant and $d\theta = 0$,

$$d\psi = \sigma \,.\, d\mathrm{S} + v \,.\, dp.$$

But $d\psi$ is a perfect differential,

$$\therefore \quad \left(\frac{dv}{d\mathrm{S}}\right)_p = \left(\frac{d\sigma}{dp}\right)_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the solution contains n grams of solute, and if u is the excess of solute in

the surface, in gms./cm.², over and above that of the bulk concentration, the concentration in the rest of the solution, instead of being n/v, will be—

$$c = \frac{n - u\mathrm{S}}{v} \text{ *}$$

or—

$$v = \frac{n - u\mathrm{S}}{c}$$

$$\therefore \quad \left(\frac{dv}{d\mathrm{S}}\right)_p = \left(\frac{dv}{d\mathrm{S}}\right)_c = -\frac{u}{c} \quad \therefore \quad \ldots\ldots\ldots \quad (4)$$

Also for dilute solutions—

$$p = \mathrm{R}\theta c$$

$$\therefore \quad dp = \mathrm{R}\theta \,.\, dc$$

and—

$$\left(\frac{d\sigma}{dp}\right)_s = \frac{1}{\mathrm{R}\theta} \cdot \left(\frac{d\sigma}{dc}\right)_s \quad \ldots\ldots\ldots \quad (5)$$

Substituting from (4) and (5) in equation (3) we have at once the required formula—

$$u = -\frac{c}{\mathrm{R}\theta} \cdot \frac{d\sigma}{dc}.$$

If the adsorbed particles are electrically charged a double layer is formed at the surface. The masses of the charged ions adsorbed have been calculated by Gibbs,† and, in a manner analogous to the above, by Professor Lewis.‡ The corresponding investigation given by Freundlich § is wrong, as, in collecting the terms expressing the work done in a cycle, the dependent and independent variables are interchanged.

DISCUSSION.

Professor Alfred W. Porter, F.R.S. : I am entirely in agreement with the authors in thinking that discussions in which the chemical potential is used are apt to be somewhat obscure, and I think that a more detailed treatment such as they give is preferable, because it is more easily understood, except perhaps by a few who have grown perfectly familiar with the potential. They make use of an infinitesimal transformation in which osmotic work $p\mathrm{d}V$ is done, and their result comes out, therefore, in the first place in terms of osmotic pressure. It is desirable, especially if a possible extension to strong solutions is in view, to obtain the result in terms of some property which has been more thoroughly studied than is the case for osmotic pressure. This can be obtained by taking the solution in contact with its vapour and making a transformation in which an infinitesimal evaporation takes place, in which case the vapour pressure replaces osmotic pressure. I have written out a simple treatment on these lines which will be printed by the Society, and have extended it to the case of strong solutions. ‖ The final result, which should be nearly exact for even very strong solutions, is very considerably different from the simple formula usually given.

* Milner, *Phil. Mag.*, 13, p. 96, 1907.
‡ *Zeit. Phys. Chem.*, 73, p. 129, 1910.
† Papers, i. 336.
§ *Kapillarchemie*, p. 186.
‖ *Supra*, p. 51.

REACTION VELOCITY IN A VISCOUS (HETEROGENEOUS) MEDIUM.

By RAPHAEL H. CALLOW.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

Up to the present little work has been done on the above subject. G. Buchböck,* dealing with the effect of neutral solutes on the velocity of hydrolysis of carbonyl sulphide, *i.e.*, solutes which have no stoichiometric relation to the reaction, gives a table containing a column of velocity constants and a corresponding column of viscosities. Using normal concentrations, the table shows that in the case of salts, with the exceptions of NaBr and LiCl, the velocity constant falls as the viscosity rises, and in the case of acids, with the exception of $CHCl_2COOH$, the constant rises as the viscosity rises. In a later research on the same subject† he used concentrations of neutral salts which in water would have been isosmotic, the freezing points of which aqueous solutions lay between −4·030° C. and −4·070° C. It was found that if the observed velocity constant was corrected for the concentration of water present the products of the new constants so obtained and the viscosities of the mixtures fell into two groups of approximately constant values.

The present work was carried out with a view to finding whether a great change in the viscosity was accompanied by a corresponding change in the order of the velocity constant. The reaction considered was the hydrolysis of methyl acetate at 18° C., the decomposition being brought about in the first case by caustic soda, and in the second case by hydrochloric acid. The concentrations of alkali or acid and methyl acetate were kept constant, and the viscosity was varied by the addition of gelatine, the viscosity being determined in a Scarpa viscometer.‡

The alkaline hydrolysis was investigated by means of the electrical conductivity,§ the concentrations of caustic soda and methyl acetate being each one-hundredth normal. In all cases where gelatine was present the velocity constant rose very rapidly as the reaction proceeded. In the first case this was due to the removal of some of the caustic soda by the gelatine as sodium salt, thus leaving an excess of methyl acetate. In subsequent cases where the gelatine was previously neutralized by caustic soda, the rise was due to the hydrolysis of the sodium salt of gelatine, thus giving excess of caustic soda. No results could therefore be obtained by this method.

Experiments were therefore undertaken, using N./2 HCl as catalyst for the ester hydrolysis. The reaction mixture was made by diluting a

* *Zeit. fur. Phys. Chem.*, 23 (1897), p. 123.
† Ibid., 34 (1900), p. 229.
‡ *Gazetta*, 40, ii. (1910), p. 261.
§ J. Walker, *Proc. Roy. Soc.*, 78, A (1906), p. 157.

mixture of 5 c.c. methyl acetate, 26·46 c.c. of 1·89 N.HCl, and the gelatine solution to 100 c.c., and 10 c.c. were withdrawn from time to time and titrated with approximately N./2 NaOH, using phenolphthalein as indicator. The reaction is monomolecular, and therefore

$$K = \frac{2{\cdot}303}{t} \log \frac{a}{a - x}$$

The following results were obtained :—

(1) *No Gelatine present.*

Time (Minutes).	Titre.	K.
0	10·42	—
31·5	11·21	$2{\cdot}245 \times 10^{-3}$
62·0	11·90	2·207
103·5	12·70	2·116
130	13·30	2·197
160	13·66	2·048
202	14·40	2·081
389	16·76	2·033
2800	22·02	—

Mean = $2{\cdot}116 \times 10^{-3}$

(2) 1·348 *per cent. Gelatine.*

Time.	Titre.	K.
0	10·47	—
29	11·10	$1{\cdot}922 \times 10^{-3}$
59	11·78	2·030
89	12·48	2·185
119	12·90	1·970
242	14·93	1·999
269	15·39	2·046
1370	21·00	[1·717]*
2880	22·10	—

Mean = $2{\cdot}025 \times 10^{-3}$

(3) 3·354 *per cent. Gelatine.*

Time.	Titre.	K.
0	10·70	—
32	11·20	$1{\cdot}663 \times 10^{-3}$
69	11·97	1·686
112	12·60	1·561
160	13·50	1·728
195	14·04	1·742
236	14·65	1·764
298	15·40	1·745
∞	22·30	—

Mean = $1{\cdot}698 \times 10^{-3}$

(4) 5·152 *per cent. Gelatine.*

Time.	Titre.	K.
0	10·46	—
42	11·28	$17{\cdot}44 \times 10^{-3}$
80	11·62	[1·318]
168	13·46	1·782
200	14·04	1·846
253	14·60	1·746
323	15·36	1·700
407	6·17	1·665
∞	2·06	—

Mean = $1{\cdot}747 \times 10^{-3}$

(5) 9·642 *per cent. Gelatine,*

Time.	Titre.	K.
0	11·55	—
124	13·59	$1{\cdot}568 \times 10^{-3}$
159	14·20	1·631
190	14·60	1·604
221	15·11	1·653
287	15·75	1·562
321	16·11	1·555
1344	21·76	1·574
2940	23·16	—

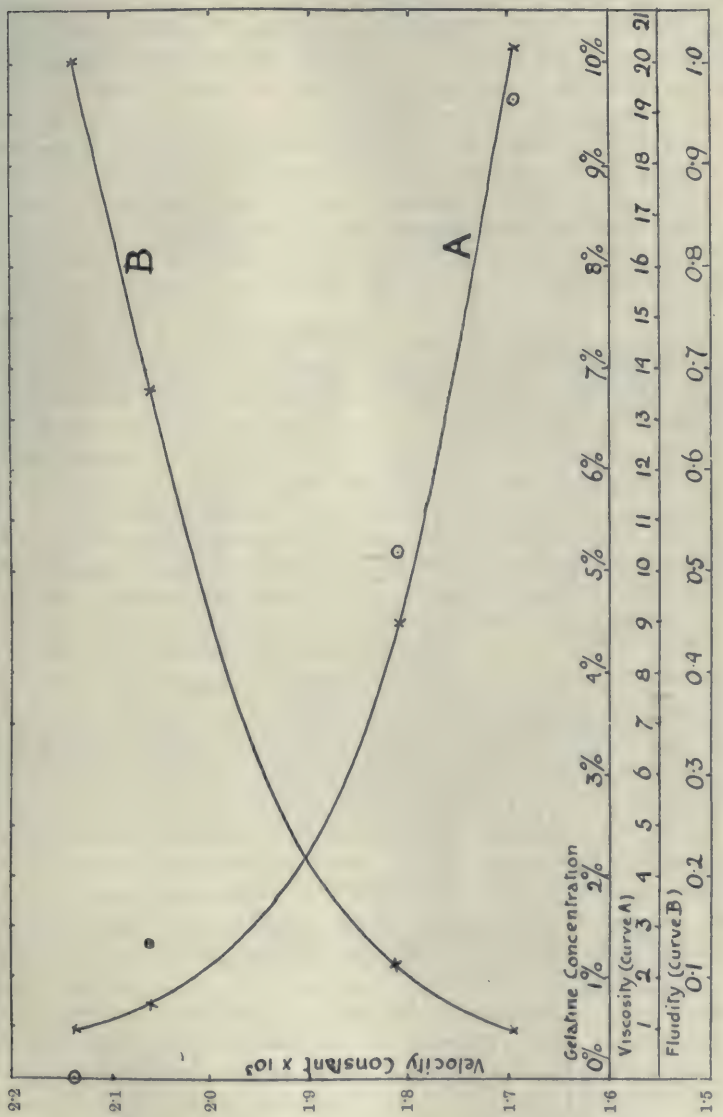
Mean = $1{\cdot}593 \times 10^{-3}$

Measurements with the Scarpa viscometer yielded the following results :—

Solution.	η relative to N/2. HCl + MeAc.
Water	0·873
N/2. HCl + MeAc	1·000
Do. + 1·348 % gelatine	1·480
Do. + 3·354 % gelatine	3·092
Do. + 5·152 % gelatine	8·976
Do. + 9·642 % gelatine	20·23 ⟶ 24·63

* Values enclosed in brackets are not included in the mean value.

The variation in the viscosity values for 9·642 per cent. gelatine was due to the solution drying in the capillary, and therefore the lower value is the more probable. The reaction was now carried out in a set jelly, and the acid used was N./5 HCl, as it had been observed that with N./2 HCl



no setting occurred, even in a solution containing 9·642 per cent. gelatine. A number of test-tubes, each containing 10 c.c. of the reaction mixture, were well corked, and hung in the thermostat. In order to titrate, the test-tube was placed in water at about 45° C. for a few seconds, and the contents were immediately shaken into about 150 c.c. of water at 30°

to 35° C. and dissolved. The whole operation took from one to two minutes, and the solution was then titrated. By this means the amount hydrolysed was negligibly affected by the rise in temperature. The viscosity could not be determined, but it was certainly of a very high order. The change in the velocity constant, however, was comparatively small. The results are given below :—

(6) Reaction mixture contained 5 c.c. MeAc + HCl, made up to 100 c.c. and titrated in portions of 2 c.c. with N./20 baryta (no gelatine present).

Time.	Titre.	K.
0	9·67	—
99	11·65	7·654 × 10^{-4}
152	12·56	7·485
216	13·70	7·570
387	16·40	7·552
1437	27·38	7·729
7389	35·90	[6·943]
17140	36·05	—

Mean = 7·598 × 10^{-4}

(7) Reaction mixture contained 5 c.c. MeAc + 9·627 grams gelatine + HCl, made up to 100 c.c. and titrated in portions of 10 c.c. with N./2 NaOH (approx.).

Time.	Titre.	K.
0	4·95	—
66·5	5·50	[9·523] × 10^{-4}
135	5·74	6·825
181	6·01	6·934
363	6·80	6·351
1400	10·10	6·078
2655	12·26	6·320
15 days (approx.)	13·94	—

Mean = 6·502 × 10^{-4}

The velocity constant must be corrected for the concentration of the water, and it was assumed that there is no volume change when gelatine dissolves in water. The density of the solid gelatine was found to be 1·911, and that of N./2 HCl was found from the tables to be 1·008, whence 100 c.c. N./2 HCl contained 98·97 grams H_2O. No correction was applied for the density of water at 18° C., which was therefore taken as unity. The volume of the gelatine was therefore subtracted from 98·97 c.c., giving the mass of water present, and the constants were related to a mass of 100 grams of water. The results are tabulated below :—

% Gelatine.		η	K. Observed.	K. Corrected.
N/2. HCl	0·000	1·000	2·116 × 10^{-3}	2·138 × 10^{-3}
	1·348	1·480	2·025 × 10^{-3}	2·061 × 10^{-3}
	3·354	3·692	1·698 × 10^{-3}	1·747 × 10^{-3}
	5·152	8·976	1·747 × 10^{-3}	1·813 × 10^{-3}
	9·642	20·23	1·593 × 10^{-3}	1·696 × 10^{-3}
N/5. HCl	0·000	1·000	7·598 × 10^{-4}	7·628 × 10^{-4}
	9·627	(Set jelly)	6·502 × 10^{-4}	6·876 × 10^{-4}

It is evident from the foregoing results that the change in the velocity constant is small compared with the change in the viscosity, especially in the case of the set jelly. The fall in the constant may be partly due to the neutralization of part of the HCl by the amino-acids in the gelatine. Such salts would be largely, but not entirely, hydrolysed in N./2 HCl, and more hydrolysed in N./5 HCl, and therefore the effect of the gelatine would be more marked in strongly acid solutions than in weaker ones, which is seen to be the case. The total fall in the constant for N./2 HCl is 20·67 per cent., and for N./5 HCl is 9·86 per cent., the concentrations of gelatine being 9·642 per cent. and 9·627 per cent. respectively. If this neutralization were the only factor affecting the constant the fall would be proportional to the concentration of the gelatine, as the amount of HCl rendered inactive would not be very large, and the relation between the velocity constant and the gelatine concentration would be given by a straight line. The points on the graph of this relation (indicated thus ⊙) are, however, too variable to allow of any curve being drawn through them.

The curve A showing the relation between viscosity and velocity constant is not simple. The shape suggests that the constant is some inverse function of the viscosity, and that the constant falls towards a limit as the viscosity rises indefinitely. This is borne out by the fact that the reaction proceeds in a jelly, where the viscosity is very large if not infinite. This can be expressed either as an exponential, or by altering Buchböck's relation $K\eta$ = constant to $(K—c)\eta$ = constant, where c is the velocity constant for the reaction in the solid state. This latter equation, however, implies that a linear relation exists between the velocity constant and the fluidity, which is not in agreement with fact, as is seen from curve B. The fall in the constant is probably due both to the neutralization and the viscosity.

No very definite conclusions can be drawn from the above work, owing to the rather large variation in the constants, the heterogeneous nature of the solutions, and the very complex character of gelatine. The shape of the curves does, however, suggest that the velocity constant is affected by the viscosity, and that some inverse relation such as an exponential or $(K—c)\eta = k$ exists between the two.

Summary.

Experiments have been carried out on the hydrolysis of methyl acetate both by NaOH and HCl in gelatine-water mixtures. With NaOH no velocity constants could be obtained. With HCl a series of constants were obtained, which showed a diminution as the gelatine concentration increased. For a large change in the viscosity, there was, however, a comparatively small change in the velocity constant. Even in the extreme case, in which the reaction proceeded in a set jelly, the velocity constant was only about 10 per cent. less than that in the case in which no gelatine was present.

In conclusion, I wish to thank Professor W. C. McC. Lewis for suggesting and directing this work.

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NOTES ON A CONVENIENT THERMOSTAT FOR ACCURATE SPECIFIC GRAVITY DETERMINATIONS AND A GAS PRESSURE REGULATOR.

By K. C. BROWNING, M.A., and C. T. SYMONS, B.A.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

The authors having had occasion to make a number of accurate specific gravity determinations,* devised a thermostat which has certain advantages over others they are aware of. The following description may be of use to those who wish to construct a thermostat, the temperature of which can be kept constant to considerably less than $\frac{1}{100}$° C.†

The thermostat (Fig. 1) consists of a heavy gauge copper tank 60 cm. long, 38 cm. deep, and 38 cm. wide. Two of the opposite sides have plate-glass windows 56 cm. long and 12 cm. deep, so that, for example, the level of liquid can be observed in a Wade and Merriman pyknometer completely immersed in the bath. The thermostat has a heavy flange fastened to it all round, 15 cm. from the top, so that it can be placed on a table, as shown in the sketch. The table is 138 cm. long, 106 cm. wide, and 92 cm. high.

The stirring is done by paddles mounted on a brass rod 15 mm. diameter, arranged horizontally near the bottom of the bath. The rod is drilled transversely and carries a number of brass paddles held in position by small milled-head set screws.

Six paddles 3 cm. × 4 cm. will be found ample to keep the water in the bath in violent agitation with a speed of 100 revolutions a minute. Lower stirring speeds were tried using larger paddles, but gave too marked oscillations in the water surface.

The rod runs in vulcanite bushes, one at each end. The bushes are conveniently held in brass bars capable of vertical adjustment by rods secured by clips at the top of the bath, as shown in the sketch.

Another method is to have the ebonite bushes mounted in detachable brass blocks fastened to the sides of the tank (near the bottom), and to adjust the chain tension by sliding the motor horizontally. On the whole this arrangement is preferable. The stirring rod is rotated by a brass chain (a pianola chain is convenient) passing over a brass wheel fixed to the rod. The chain is driven by another chain wheel mounted on a spindle clipped to the top edge of the bath. It is important to use wheels with cut gears and not with pins for teeth. The cut gears will last out several sets of pin teeth wheels.

The spindle is conveniently driven through a spring coupling attached to an electrically-driven worm reduction gear (a spring coupling about

* "Alcohol Estimation in the Tropics," *J. Soc. Chem. Ind.*, August, 1914.

† *A detailed working drawing of the apparatus is available on application to the Secretary of the Faraday Society.*

4 cm. long is ample). This obviates a number of pulleys and unsatisfactory string drives.

A suitable motor with worm reduction gear is supplied by the General Electric Company ($\frac{1}{10}$ h.p.). The speed is regulated by a resistance

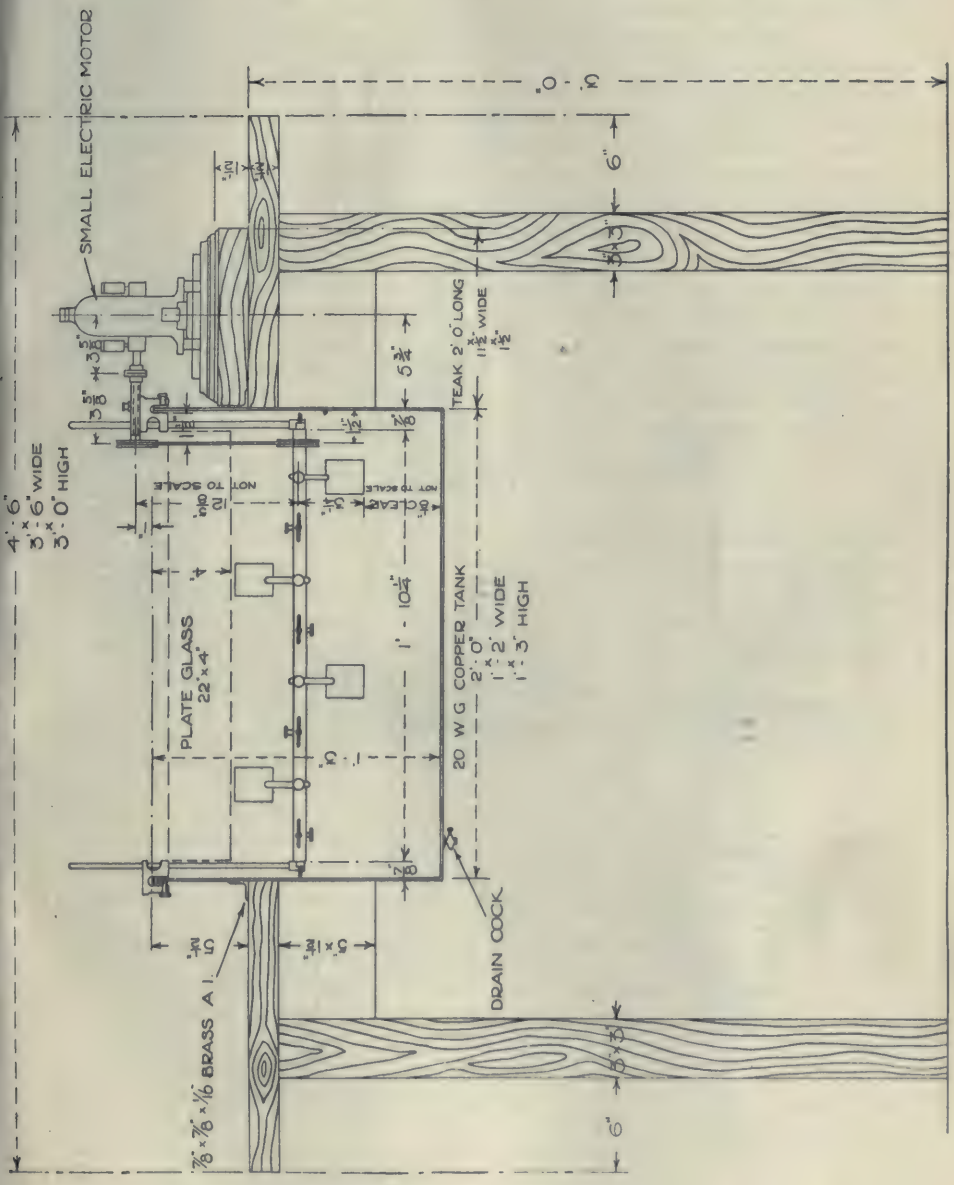

FIG. 1.

or with alternate current motors by a choking coil fixed on the table. The motor and worm gear are mounted on a block by the tank.

The heating can be done by gas (controlled by a Lowry thermo-regulator), or electrically.

An easy method of electrical heating is to fuse a heavy platinum wire into the bottom of a Lowry thermo-regulator. This is, of course, in contact with mercury. The other contact is a platinum wire mounted on a long thin brass rod, and the position of which is regulated by a fine

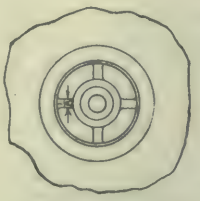

FIG. 3.—Plan of Valve-Seat.

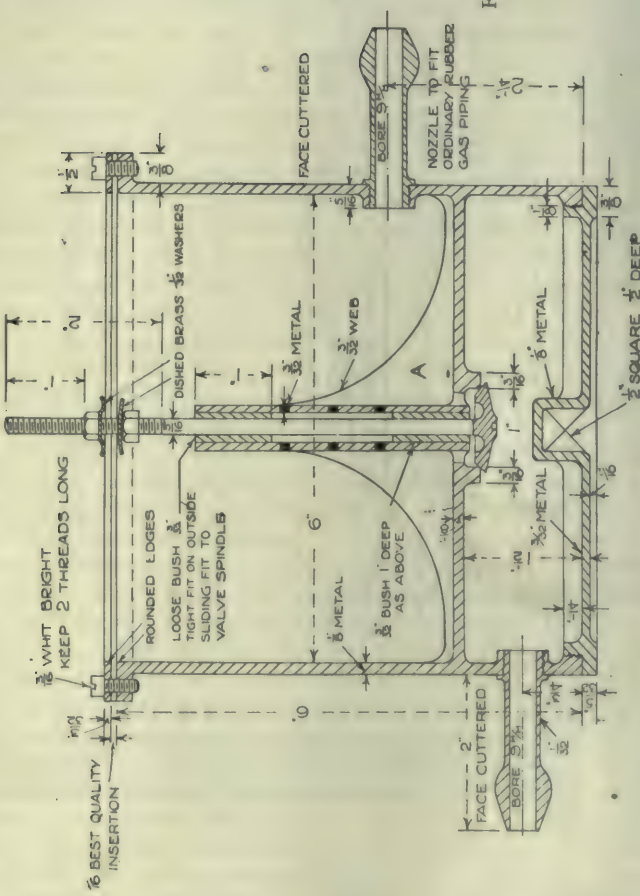

FIG. 2.—Manostat used between Gas Supply and Bunsen Burner.

thread cut on it, as shown in the sketch. A four-volt accumulator is in series with the mercury thread and platinum point and a relay. When contact is made, the relay turns off part of the heating current.

The easiest method is to arrange the heating current to be just enough

to keep the bath a few $\frac{1}{100}$° C. below the working temperature, and to let the relay switch on and off a small extra heating current.

By shunting the platinum and mercury contact with a pair of aluminium plates, each of about 12 sq. in., insulated by glass tubing from each other and immersed in distilled water, sparking is decreased so much that no visible fouling of the mercury takes place for weeks.

The gas pressure regulator (Fig. 2) consists of a brass cylindrical casting, walls 3-4 mm. thick, 16 cm. internal diameter, and about 16 cm. high. Near the bottom is a brass partition which carries the valve bush and seating. The bottom is a heavy brass plate screwed into the cylindrical casting. It is provided with a squared recessed boss in the centre. The recess takes a key which is used to unscrew the bottom and enable the valve to be got at for grinding in when necessary. The top consists of a sheet of rubber insertion held in position by a brass ring, screwed by 16 screws into a flange. Through the centre of the rubber insertion passes the valve stem. It is secured by two nuts and concave-convex brass washers. A large brass washer 11 cm. in diameter is placed above the rubber insertion, as shown in the sketch. The concavity of the washers is slight and should be such as to let the rubber insertion fit snugly to the washers when it is raised a little. At the top of the valve stem is a cup, in which weights can be placed.

The two essential parts of the design are :—

1. *The valve and seating* (Fig. 3). The valve must move freely and the stem be dead true. The contact between the valve and seating must be very *narrow*. A wide contact surface cannot be kept true, and always leaks after a little use. The valve is ground into its seating with 220 mesh carborundum powder and finished with FF carborundum. Grinding is rarely required.

2. *The large concave-convex washer* (Fig. 2). If this is not used, the valve stem is apt to stick in its bushing, owing to the slightly irregular movement of the rubber insertion.

The advantages of this regulator are :—

1. It does not leak either at the valve or at the flexible top. If a gas pressure of 30 in. water be applied at the inlet, a water gauge at the exit will not alter its level perceptibly when the pressure at the inlet is maintained for half an hour.
2. It is portable and takes up little room.
3. It can be rapidly set for any desired reduction of pressure.
4. It does not require careful levelling and is very strong.

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A NEW METHOD FOR DETERMINING THE SPECIFIC HEATS OF LIQUIDS.

By E. J. HARTUNG, B.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

In the course of a research on certain thermal properties of binary liquid mixtures it was found necessary to measure the specific heats of a large number of liquids. It was therefore very desirable to have a simple, rapid, and reasonably accurate method of measurement. The following paper contains an account of a new method for determining the specific heats of liquids, which has been found very suitable for the purpose named. It has the added advantage of requiring a relatively small quantity (60 c.c.) of the particular liquid for a determination. The method retains the simplicity of the old mixture method for measuring specific heats while greatly diminishing its serious errors.

The initial idea, from which the method was worked out, was supplied by Professor Orme Masson, who suggested that the liquid in question be cooled by the application of a known weight of dry ice sealed up with a roll of silver gauze in a thin glass bulb. This suggestion was acted upon, and, after suitable apparatus had been constructed, good and consistent results were obtained. The method in brief consists in freezing the bulb containing the water in a suitable apparatus and then introducing the bulb into the liquid in the calorimeter and noting the fall in temperature.

Description of Apparatus.

The apparatus consists of three parts : 1, the ice carrier ; 2, the freezing apparatus ; 3, the calorimeter.

The Ice Carrier (Fig. 1).—This consists of a small, cylindrical, thin glass sealed bulb, containing from 1 to 3 c.c. of pure water and as large a roll of silver gauze as possible. The respective masses of the glass, the water, and the silver are accurately known. The bulb is furnished with a small glass hook, to which is attached a fine platinum wire suspension. The silver gauze ensures rapid melting of the ice in the bulb when this is introduced into the calorimeter, and also makes the bulb heavy enough to sink in dense liquids. Sufficient free space must be left in the bulb to allow for the expansion of the water when freezing. It is convenient to make several ice carriers of different sizes.

The great advantage of these ice carriers, when compared with the previously used hot metals, etc., in mixture methods, lies in their small size and great "cold" capacity. Thus, a bulb containing 3 grams of ice, when rising in temperature from 0° to 20°, absorbs well over 300 calories.

The Freezing Apparatus (Fig. 2).—This consists of a glass tube (4 cm.

diameter and 15 cm. long) containing about 100 c.c. of clean dry mercury (E). It is closed by a well-fitting rubber stopper (A), which is perforated in the centre by a hole wide enough to allow the largest ice carrier in use to slip easily through. A standard thermometer (B), graduated to tenths of a degree, is provided with a small rubber cork, which fits this hole closely and allows the thermometer to dip into the mercury. The ice carrier is held under the mercury by means of two glass rods (C) passing through the stopper. The ends of these rods are so shaped that a partial rotation of one rod above the stopper releases the carrier. A small calcium chloride tube (D) passes through the stopper and enables a stream of dry air to be drawn through the apparatus.

The carrier is withdrawn from the tube through the central hole in the

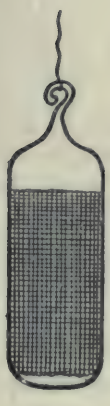

FIG. 1.

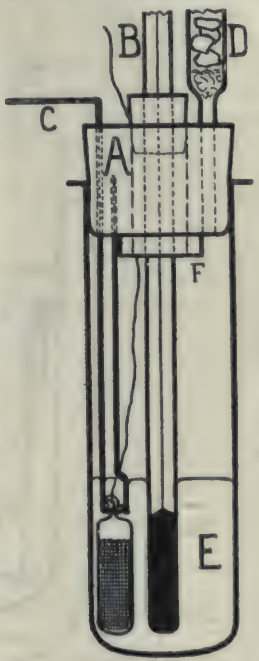

FIG. 2.

stopper after the removal of the thermometer. In order to ensure that no mercury adheres to the bulb, a thin perforated cardboard disc (F) is fixed just below the stopper. The perforation in this disc is lined with feather tips gummed to the cardboard and all pointing inwards. The carrier, in passing through the disc, is thoroughly wiped by the feathers and emerges from the tube quite clean.

The mercury tube fits into a wider glass tube which acts as an air jacket. The whole can be cooled in the usual bath of brine and ice.

The Calorimeter (Fig. 3).—This consists of a thin-walled cylindrical metal vessel (A) (4 cm. diameter and 8 cm. depth) provided with a flanged edge and made preferably of platinum. The calorimeter used in these experiments was made of thin sheet copper, well silvered internally, and weighed 27 grams. The calorimeter is supported inside a silvered Dewar tube (B) (inner dimensions 5 cm. diameter and 12 cm. depth) by means of a rubber ring (C) (made

from thick-walled tubing) encircling the calorimeter just below the flange. This ring fits tightly the inner jacket of the Dewar tube and rests securely on a ring of cardboard (D) gummed round the inside of the tube. The mouth of the tube is closed by a 5 cm. rubber stopper (E), which reaches to within a short distance from the top of the calorimeter. This leaves only a small space above the calorimeter in which the contained liquid can vaporize. The under surface of the stopper is protected from vapours by several layers of tinfoil. Through the stopper passes a previously calibrated and standardized Beckmann thermometer and a thin glass stirring-rod (H), the lower end of which is suitably shaped to receive the ice carrier used. The stirrer is lubricated through the stopper with a little vaseline or phosphoric acid. The carrier itself is introduced into the calorimeter through a hole in the stopper lined with a short piece of glass tubing and closed with a small well-fitting rubber

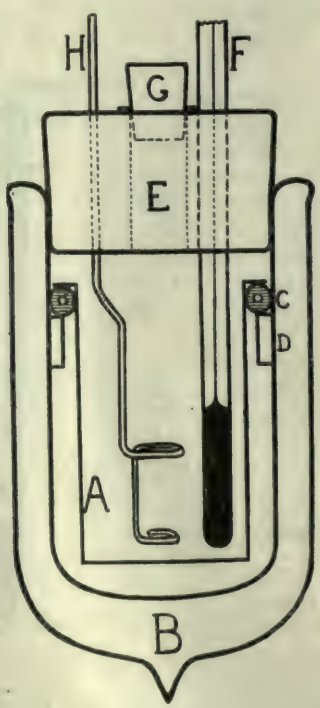

FIG. 3.

stopper (G). The liquid to be experimented with is also introduced through this hole. The position of the stirring-rod can easily be arranged so that the carrier, on being introduced into the calorimeter, invariably slips into its place in the stirring-rod.

The Dewar tube is shielded from external radiations by being placed in a double-walled cylindrical wooden box packed with wool and provided with a separate perforated cover.

The Method of Experiment.

The liquid to be experimented with is put into a weight pipette and allowed to attain the room temperature. About 60 c.c. are then introduced

into the calorimeter, and the latter is then closed and allowed to stand, with occasional stirring, until the temperature is constant, or at most changes very slowly. In the meantime, the selected ice carrier is secured under the mercury in the freezing-tube, and a current of dry air drawn through the apparatus for some minutes. This prevents any condensation of water inside the tube during the freezing. The standard thermometer is then inserted and the tube surrounded with a bath of brine and ice at about $-5°$. Freezing of the water in the carrier takes place easily and rapidly. After a few minutes, the tube is removed, placed in its jacket, and surrounded with a second bath of brine and ice at approximately $-1°$ until the temperature of the mercury is constant. This usually takes about 10 minutes.

The temperatures in the calorimeter and the freezing apparatus are read. The thermometer is then removed from the latter, the bulb withdrawn by its suspension, and introduced into the stirring-rod in the calorimeter, which is then immediately closed again. These operations can be very rapidly performed, and little gain of heat by the bulb can result. The time is noted and hand stirring started, until in from two to three minutes the well-defined minimum temperature is reached. In order to correct for radiation errors, the rise in temperature for an equal interval is then noted. The water equivalent of the apparatus is previously determined, using distilled water as the contained liquid. All the data necessary for calculating the specific heat of the liquid are then known.

It has been found that the water equivalent of the apparatus varies to some extent with the time of experiment. This is specially noticeable if a thin glass calorimeter is substituted for the metal vessel, and is principally due to the poor conducting powers of glass. However, the variation is regular, and a graph is easily constructed which enables the water equivalent values, corresponding to the times of experiment, to be read off at once.

Occasionally a very small globule of mercury is introduced into the calorimeter with the ice carrier, but the amount is quite negligible. It is very convenient to perform the measurements in a room kept at approximately constant temperature. This obviates the continual standardising of the Beckmann thermometer with every change in the room temperature.

Results Obtained.

Several series of water equivalent determinations gave results not differing amongst themselves by more than 0·4 per cent.

In order to test the apparatus, a series of specific heat measurements of mixtures of pure sulphuric acid and water were made, and the results were compared with the figures obtained for these mixtures by J. Thomsen.* For this purpose a thin glass calorimeter was used. The measurements were made between $17°$ and $20°$. The sulphuric acid used was a fresh sample of Schuchardt's pure 1·84 sp. gr. acid. This acid was found to be free from oxides of nitrogen and to leave on evaporation only the slightest residue. Various mixtures were made up with distilled water in glass-stoppered flasks and the density (at $20°$) and specific heat of each mixture measured. By reference to tables in Landolt's *Physikalisch-chemische Tabellen*, fifth edition, the compositions of the mixtures were calculated from the densities. The following table gives the actual results which were obtained, compared with the corresponding values taken from Thomsen's smoothed curve. The compositions of the solutions are given in the column headed "N," this denoting the number of molecules of sulphuric acid in one total molecule of solution.

* *Thermochemistry*, J. Thomsen, Ramsay Physical Chemistry Series, p. 161.

TABLE I.

N.	Specific Heat (Ice Method).	Specific Heat (Thomsen).
0·0115	0·947	0·949
0·0236	0·909	0·904
0·0451	0·842	0·835
0·0566	0·807	0·802
0·0786	0·751	0·745
0·107	0·681	0·685
0·142	0·615	0·619
0·171	0·574	0·577

Good agreement is shown between the two sets of results.

In the course of subsequent work, measurements were made on a series of pure liquids, but, owing to the very unsatisfactory nature of the available specific heat data for the majority of pure liquids, no proper comparisons can be made. The following table gives the results obtained between 17° and 20° ; the methods of purification of the liquids are held over for a subsequent paper.

TABLE II.

Liquid.	Specific Heat.
Methyl alcohol	0·591
Ethyl alcohol...	0·564
Ethyl ether	0·541
Carbon disulphide	0·234
Aniline...	0·472
Nitrobenzene...	0·342

In conclusion, the method described is simple, rapid, and appears to be reasonably accurate.

The author expresses his sincerest thanks to Professor Orme Masson and Mr. F. H. Campbell, M.Sc., for their kindly interest and advice.

CHEMISTRY DEPARTMENT, MELBOURNE UNIVERSITY,
December, 1914.

AN ELECTROMAGNETIC VACUUM BALANCE.

By JOHN S. ANDERSON, M.A., B.Sc., Ph.D.,

Assistant Lecturer in Physics, University of Birmingham, late 1851 Exhibition Scholar (Glasgow).

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

During the course of work * carried out by the author on the rates of absorption and giving up of water, alcohol, and benzene vapours by a gel of silicic acid a balance was designed to allow of substances being weighed *in vacuo*. The chief aim in designing the balance was to be able, if possible, to weigh a substance, whose weight may alter under certain conditions, from time to time without removing it from the vacuum. Such a substance we have in the gel of silicic acid, which is a porous solid capable of absorbing considerable quantities of water and other liquids. When a dried silicic acid gel is brought into an atmosphere of water vapour, the minute pores of the gel rapidly become filled with condensed vapour owing to capillary action. If the weight of the gel and the absorbed water can be rapidly and accurately measured from time to time, the velocity of absorption may easily be determined.

In the first method * adopted by the author of measuring the rates of absorption of the vapours of water, alcohol, and benzene by a silicic acid gel, a portion of the gel was placed in a special vessel which was brought into communication with a vacuum apparatus containing concentrated sulphuric acid. The whole apparatus was evacuated and the vessel containing the gel was removed from time to time and weighed on an ordinary chemical balance until the weight remained constant, the gel being then dry. The vessel was next brought into communication with a vacuum apparatus containing water, and was removed, weighed, and replaced from time to time. From the weight thus found the amount of water absorbed by the gel at any time was easily determined.

This process was, however, found to be rather tedious and inconvenient, so an attempt was made to simplify the method of measurement. For this purpose an electromagnetic vacuum balance, which we shall now describe, was designed. The principle involved is that of the well-known Kelvin balance for "weighing" electrical currents.† One of the scale-pans of an ordinary balance is replaced by a circular coil of wire whose axis is vertical. This coil is movable between two larger fixed coils of wire, which have the same vertical axis. The three coils are so connected that an electrical current

* J. S. Anderson, *Die Struktur des Gels der Kieselsäure*, Inaug.-Diss., Göttingen, 1914, Anhang iii ; *Zeitschrift f. phys. Chemie*, 88, 191 (1914), Anhang ii.

† A vacuum micro-balance, depending on the same principle, but of quite a different design, is described by M. G. Urbain, *Comptes Rendus*, 6, 347 (1912).

may be passed through them in series, through the movable coil and the lower fixed coil in one direction and through the upper fixed coil in the opposite direction. Thus when an electrical current is passed through the coils, the movable one is attracted towards the lower, and repulsed by the upper, fixed coil. These attractive and repulsive forces may be increased or decreased by increasing or decreasing the current passing through the coils; they are made use of to counterbalance the force of gravity acting on the substance to be weighed in the scale-pan hanging from the other end of the beam of the balance. Should the weight of the substance vary from time to time, the variations can be determined by altering the current passing through the coils until equality of the forces acting on either end of the balance beam is obtained. The balance is enclosed in a bell-jar which can be evacuated, so that the process of weighing can be carried out while the substance whose weight is required is in a vacuum.

The balance was constructed according to the author's designs by Messrs. Spindler and Hoyer, Göttingen, Germany. The beam of the balance and the parts appertaining to it were obtained from Messrs. Sartorius, Göttingen. Fig. 1 shows a front view of the balance, the bell-jar cover being removed. The chief metallic parts are nickel-plated. A is the scale-pan in which the substance to be weighed is placed. B is the movable coil of wire which takes the place of the second scale-pan. It hangs halfway between the fixed coils of wire B′ and B″ when the beam C is at rest, that is, when the pointer D is at zero. The knife-edge at the centre of the beam C rests on a small plate of agate. The balance is fixed to a round glass plate E which lies on a steel table E′ having three legs. This table rests on a wooden board, to which are attached three screws, the height of which may be varied at will. By adjusting the screws the plate on which the balance rests may be fixed in a horizontal position. The height of the beam C above the glass plate E is about 22 cm. The dimensions of the movable parts of the balance are such that the total surface exposed on either side of the beam is approximately the same. The reason for this is that when in an experiment water vapour, or other vapour, is introduced into the balance, there will be approximately the same amount of vapour adsorbed by the metal, glass, etc., on either side of the beam.

The method of connecting up the coils of wire B, B′, and B″ with one another and with the necessary battery is as follows: Two brass terminals F′ and F″ pass through small holes in the glass plate E. In order to prevent leakage of air at the terminals when the bell-jar cover is on the balance and the apparatus is evacuated, small leather washers are provided above the plate E, and the terminals are sealed below the plate by means of wax. A little rectangular box of ebonite G (seen better in Fig. 2) is fixed to the beam C at the top of the pointer D. This box is divided into two compartments, each containing a little mercury. Above the box, and attached in a horizontal position to the centre of the beam, is a small rod of ivory H′. Two small pieces of platinum I′, I″ passing through this rod are fixed vertically in such a position that each of them dips into one of the mercury compartments of the box G. When the beam vibrates about its position of equilibrium the pieces of platinum move through the mercury, but friction is reduced to a minimum owing to the fact that the lower ends of the platinum pieces are very fine and are slightly flattened in the planes of motion. On the end of the balance beam from which the coil B hangs is fixed another small ivory rod H″. Two very fine wires are stretched from the pieces of platinum I′, I″ over the rod H″ and pass down in the form of spirals K′, K″ to the two ends of the movable coil B. Wires connect the terminal F′ and one of the compartments

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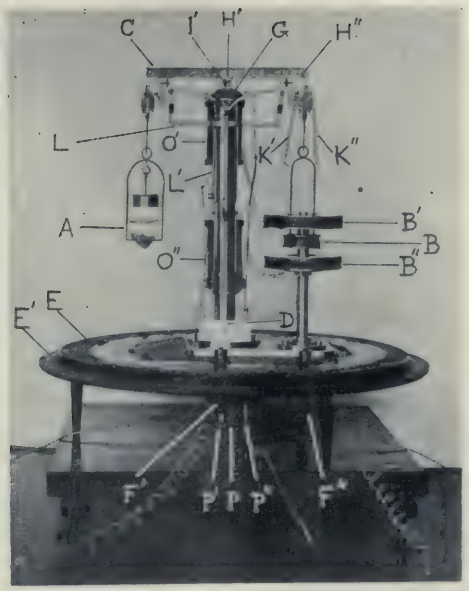


FIG. 1.

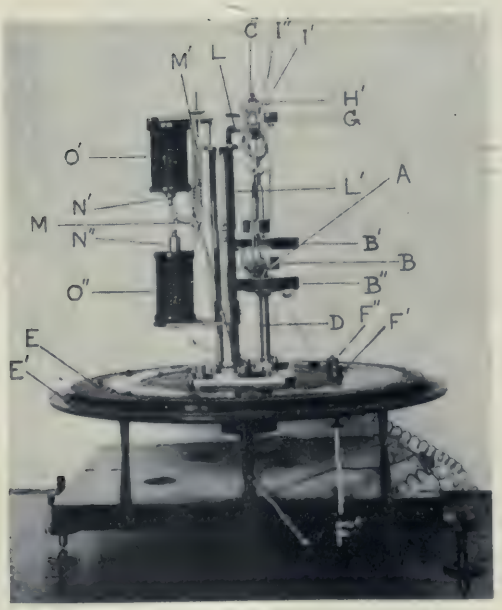


FIG. 2.

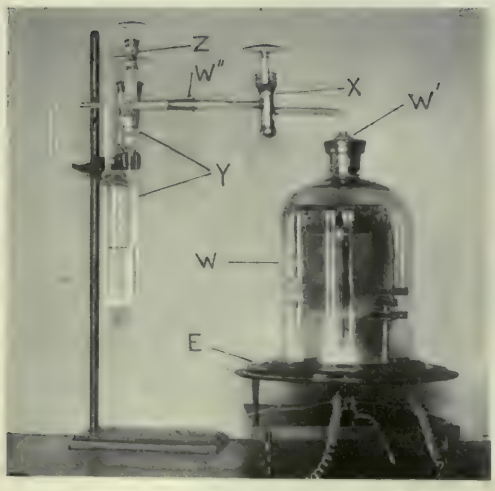


FIG. 4.

of the box G, the terminal F'' and the coil B'', the coil B'' and the coil B', the coil B' and the other compartment of the box G. Thus there are electrical connections from the terminal F' through the mercury in one of the compartments of G, the piece of platinum I' and the wire K' to the coil B and back through the wire K'', the piece of platinum I'' and the mercury in the other compartment of G to the coil B' and thence through the coil B'' to the terminal F''.

When the balance is not in use the beam C rests on the framework L. The method of releasing and fixing the beam may be seen from a study of Fig. 2, which gives a side-view of the balance, the bell-jar cover being removed. M is a lever at the back of the balance. The outer end of it is connected above and below by two metal pieces to two cylindrical iron rods N', N'', which can move freely in a vertical direction inside the two solenoids O', O'' fixed to the central upright stem of the balance. When a current of

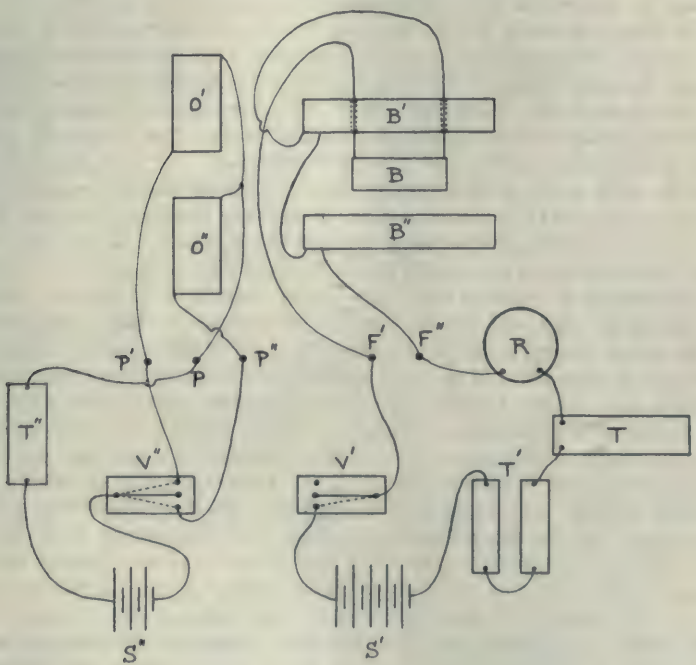


FIG. 3.

electricity is passed through the coil of the lower solenoid O'' the iron core N'' is drawn down into the solenoid. Thus the outer end of the lever M is drawn downwards, allowing the cylindrical shell L' and the framework L which is connected to it to fall down a short distance, the balance beam C being thus released. The weight of the cores N', N'' causes the lever M to remain down when the current is switched off. When an electrical current is now passed through the coil of the upper solenoid O' the iron core N' is drawn upwards. This action causes the outer end of the lever M to rise, thus raising the cylindrical shell L' and the framework L. The beam C is therefore held fixed at rest again. A wire spring M' holds up the lever M when the current is switched off. Thus in order to release or fix the beam of the balance, a

current of electricity need only be momentarily passed through the lower or the upper solenoid.

Three wires, insulated from one another by means of ebonite, pass through the metal base of the balance and through the glass plate E. They end below the steel table G in three terminals P, P′ and P″ (Fig. 1). One end of the coil of wire in the solenoid O′ is connected to the terminal P′, one end of the coil in the solenoid O″ is connected to the terminal P″, while the other ends of the coils are both connected to the middle terminal P.

The electrical connections necessary for operating the balance are shown diagrammatically in Fig. 3. To the right of the figure are the connections for the movable coil B and the fixed coils B′ and B″. As before, F′ and F″ are the terminals on the under side of the glass plate E (Fig. 1). The connections below F′ and F″ are all outside the balance; the others have already been described. R is an ampere-meter for measuring the current passing through the coils. The battery S′ gives a pressure of about 70 volts. T is a resistance box and T′ represents two slide-resistances connected up in series. V′ is a key by means of which the circuit may be made or broken at will. To the left of Fig. 3 are shown the connections necessary for releasing and fixing the balance beam by means of the lever operated on by the solenoids O′ and O″ and their iron cores. As in Fig. 1, P, P′, P″ are the three terminals projecting under the metal table on which the balance rests. The battery S″ gives a pressure of about 10 volts. T″ is a slide-resistance. V″ is a two-way key; when the lever is placed in the upper position (dotted line) the circuit through the upper solenoid O′ is closed, and when placed in the lower position (dotted line) the circuit through the lower solenoid O″ is closed. When the lever is in the middle position no current passes through either circuit.

The method of working with the vacuum balance is as follows. By way of example we may take the case where it is desired to make measurements on the rate of absorption of water vapour by a gel of silicic acid. Some small pieces of the gel are first of all dried carefully in a desiccator over concentrated sulphuric acid. They are then placed in a glass dish which rests on the scale-pan A (Fig. 1) of the balance. Weights are then added to the scale-pan until the total weight on this side of the beam is somewhat greater than the weight of the movable coil B on the other side. If this condition is satisfied, a small electrical current must be passed through the coils B, B′ and B″ in order to compensate for the extra weight, and thus bring the pointer D to the zero mark when the beam C is released. A bell-jar cover is next placed over the balance. The lower rim of the cover was originally ground on the glass plate E when the balance was constructed, before the balance was attached to the plate. When the rim is smeared with a little "Ramsay" fat and the cover is placed on the glass plate and turned round once or twice, a good seal is obtained between the rim and the plate.

The vacuum balance, as it appears in use, is shown in Fig. 4. All the electrical connections are not, however, shown. The two coiled wires are for connecting up the circuit through the movable and fixed coils, the forces of attraction and repulsion between which compensate for the weight of the substance in the scale-pan. The other three wires shown in the figure are for connecting up the solenoid circuits for releasing and fixing the beam of the balance. W is the bell-jar cover, the lower rim of which fits closely on to the glass plate E. The hollow stopper W′ is prolonged into a horizontal tube, the end W″ of which is ground to a standard size, obtainable from Messrs. Leybold, Nachfolger, Cologne. The tube is provided with a mercury-seal tap X. The end W″ fits into the side tube of a vacuum apparatus Y used in connection with the dehydration and rehydration of silicic acid gels. This

apparatus, which has already been described,* consists essentially of a vessel having a capacity of about 300 c.c.; it is provided with a mercury manometer and with two vacuum taps. It may be evacuated through the side tube Z. This form of apparatus is not essential for work with the vacuum balance, but it has been found very convenient in connection with the measurement of the velocities of absorption of vapours by silicic acid gels.

In the case of measurements with water vapour, the vessel of the vacuum apparatus Y is first of all about half-filled with concentrated sulphuric acid. The whole apparatus is evacuated by means of a pump,† the pressure being registered on the mercury manometer. The weight of the silicic acid gel in the scale-pan of the balance is found by measuring with an ampere-meter the current that must be passed through the coils in order to bring the pointer to zero, the variation of current with weight being previously determined by

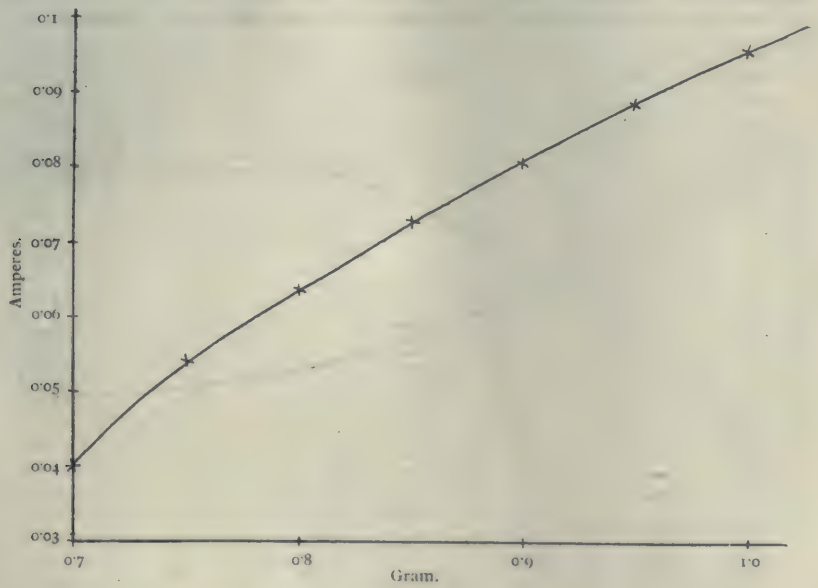


FIG. 5.

calibrating the balance. The measurements are carried out from time to time until the necessary current reaches a steady minimum value, thus indicating that the gel is as dry as it is possible to obtain it over concentrated sulphuric acid. The tap X is then closed, and the sulphuric acid in the apparatus Y is replaced by water. When Y has been evacuated as far as possible, the tap X is opened, thus allowing the whole apparatus to be filled with water vapour. At fixed intervals after the tap X is opened the current necessary to bring the pointer of the balance to the zero mark is measured. Owing to the absorption by the gel of water vapour, which condenses in the pores of the gel, the requisite current of electricity increases with the time until a maximum is reached. This maximum current corresponds to the

* R. Zsigmondy, W. Bachmann u. E. F. Stevenson, *Zeitschrift f. anorg. Chem.*; 75, 189 (1912); J. S. Anderson, Inaug.-Diss., Göttingen, 1914.

† In the experiments carried out by the author a Gaede rotary capsule pump was employed.

condition that the pores of the silicic acid gel are completely filled with water.

The whole process may then be reversed, the water in the apparatus Y being replaced by concentrated sulphuric acid. The current that must be passed through the coils in order to bring the pointer of the balance to zero will decrease in strength with the time until a minimum value is again reached, corresponding to the condition in which the gel is again dry.

The balance should be carefully calibrated before and after a series of experiments. This may be done by placing certain known weights in the scale-pan of the balance and determining the strengths of the currents that must be passed through the coils in each case. A curve may then be constructed, giving the relation of electrical current to weight. From the measurements made in the case of the absorption and giving up of water vapour by the silicic acid gel, the weight of the gel and the water it contains at each time of measurement may easily be determined by reference to the curve.

The results of one series of measurements may be given here by way

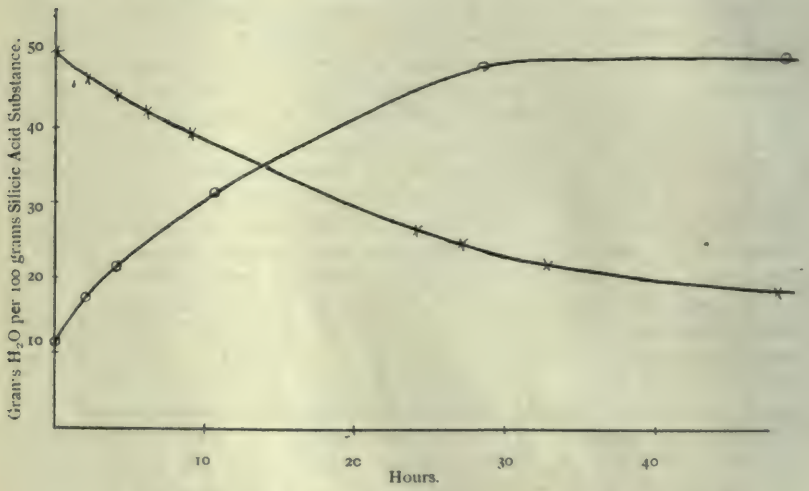


FIG. 6.

of illustration. The calibration curve for the range of weights used is given in Fig. 5. The abscissæ represent the weights in the scale-pan and the ordinates give the corresponding current strengths in amperes. With the ampere-meter used in the experiment a difference of 0·1 milliampere could be detected. This corresponds to a difference in weight of 0·35 to 0·7 milligram, depending on the portion of the range of weights used. If more care were to be taken in choosing the range of weights, and if a more accurate ampere-meter were employed, it would be possible to increase the sensitiveness of the balance considerably. Although the beam of the balance is capable of carrying weights up to about 100 grams, only about 0·75 gram silicic acid gel was employed in the experiment. If a greater amount of the gel were employed, more water would be absorbed, and therefore a greater range of electrical current would have to be made use of. It is advisable to determine approximately before an experiment what the total variation in weight of the substance under examination will be, so that a convenient range of

current may be employed. The maximum current applied should be kept fairly small, in order to prevent heating of the coils.

The results of the measurements with water vapour are shown graphically in Fig. 6. The abscissæ represent the times that have elapsed since the beginning of the experiments, and the ordinates give the corresponding amounts of water in the pores of the gel, reckoned as grams of water per 100 grams of the silicic acid substance.* The curves are similar to those obtained according to the first method adopted by the author.† In the present case, however, the drying process was not carried out so far, the reason being that the Gaede pump employed was not in the best working order when the measurements were made.

The above measurements, although not representing the maximum accuracy obtainable, serve to show how the vacuum balance may be applied to the measurement of the velocities of absorption of vapour or gas by such porous substances as silicic acid gels. There are numerous other physical and chemical processes which may be investigated with the help of the balance. Further experiments are at present being carried out by Mr. Varga in the Laboratory for Inorganic Chemistry in Göttingen.

In conclusion, the author wishes to express his heartiest thanks to Professor R. Zsigmondy, Göttingen, for the kind interest he has taken, and the help he has given, in connection with the vacuum balance.

* Cf. J. S. Anderson, Inaug.-Diss., Göttingen, 1914, p. 21

† Loc. cit., Anhang iii.

NOTE ON THE NEUTRALIZATION CURVE OF BORIC ACID.

By E. B. R. PRIDEAUX, M.A., D.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

During an investigation into the possibility of titrating boric acid directly, a peculiarity was noticed in the course of the neutralization curve, which expresses the ratio equivalents of added alkali to mols of acid (R) as a function of the hydrion concentration. As there appears to be no inflection in the curve after the point NaH_2BO_3 has been passed, the whole course of neutralization should be expressible by means of the single constant of a monobasic acid, using the formula—

$$R = \frac{1 + \frac{Kw}{[H^{\cdot}]\, a_2\, [NaH_2BO_3]}}{1 + \frac{[H^{\cdot}]\, a_1}{K}}$$

In which a_1 refers to the primary dissociation of NaH_2BO_3 and a_2 to that of NaOH.

If the dissociation constant of Walker, $K = 1{\cdot}7 \times 10^{-9}$, is used, a_1 and a_2 are put equal to 0·8 and 0·9 respectively, the following values are obtained for a 0·2 molar solution :—

$-\log [H^{\cdot}]$	=	4·73	6	7	8	9
R	=	0·00	$0{\cdot}0_32$	0·021	0·075	0·68
$-\log [H^{\cdot}]$	=	10	11	12		
R	=	0·955	1·002	1·07		

The following have been obtained by Sorensen using the hydrogen electrode :—

$-\log [H^{\cdot}]$	=	6·55	7·62	7·94	8·14	8·29	8·51
R	=	0·0	0·048	0·09	0·13	0·17	0·23
$-\log [H^{\cdot}]$	=	8·68	8·80	8·91	9·01	9·09	9·17
R	=	0·29	0·33	0·375	0·41	0·45	0·475
$-\log [H^{\cdot}]$	=	9·36	9·50	9·90	9·91	9·98	
R	=	0·555	0·625	0·715	0·83	1·00	

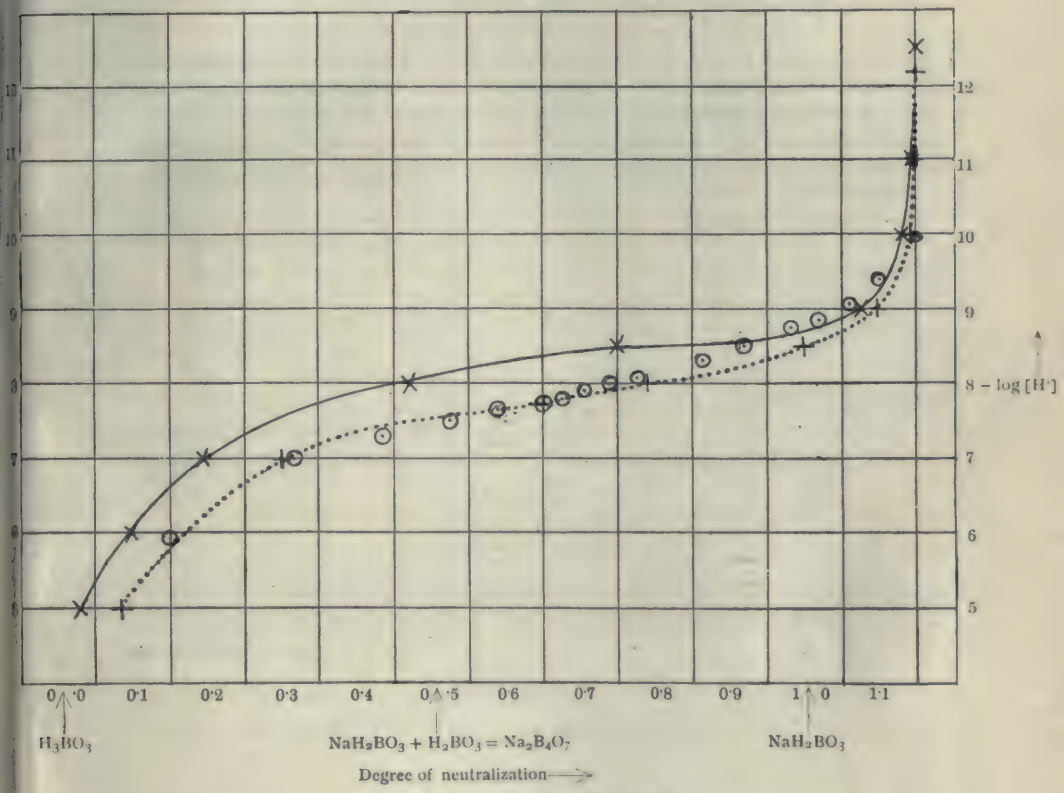
It is evident that the theoretical points (+ + in the diagram) do not agree with the experimental (⊙⊙). A reason for this discrepancy is probably to be found in the formation of complex ions. Boric acid itself has little tendency to complex formation. Thus the van't Hoff coefficient, representing the number of gram molecules in solution derived

from one formula weight is found to be 1·02 to 1·04 by different methods.*

The formation of complexes in borate solutions will cause a difference between the apparent dissociation constant in these and the constant of the pure acid. The ion H_2BO_3' will be weighted with these complexes, since in the solutions containing alkali the reaction has taken place—

$$n\,H_2BO_3 \rightleftarrows (H_2BO_3)_n' \cdots n$$

The apparent will be less than the true dissociation constant, and if the



Neutralization of Boric Acid.

Abscissæ = Equivalents of alkali to 1 mol of acid.
Ordinates = Values of $-\log[H^+]$.

× × Plain curve calculated from $k = 1{\cdot}7 \times 10^{-9}$.

+ + Dotted curve calculated from $k = 4{\cdot}5 \times 10^{-10}$.

○ ⊙ Experimental values (Sorensen).

former does not alter much with the degree of neutralization, it may be obtained from the experimental values.

At the ratio 0·5 ($NaH_2BO_3 + H_2BO_3$, or borax)

$$-\log[H^+] = 9{\cdot}25$$

* Wildermann, *Zeitsch. f. phys. Chem.*, 42, 488

Hence—

$$\frac{K}{a_1} = 5{\cdot}62 \times 10^{-10}$$

and if

$$a_1 = 0{\cdot}8,\ K = 4{\cdot}5 \times 10^{-10}$$

or about one-sixth of the true constant.

The values recalculated with this constant are as follows :—

$= -\log [H^{\cdot}]$	=	4·82	6·0	7	8	9	10
R	=	0·0	$0{\cdot}0_35$	0·005	0·043	0·31	0·82
$= -\log [H^{\cdot}]$	=	11	12				
R	=	0·985	1·065				

In the first part of the curve the revised K gives too great an alkalinity, as would be expected if the degree of complex formation increased with that of neutralization. The former, however, appears to reach its maximum soon, and the revised K may be used to calculate accurately the alkalinity for borate regulator mixtures up to strongly alkaline solutions.

ON THE ANODIC SOLUTION OF LEAD.

By NORMAN MURRAY BELL.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

Introduction.—As a result of recent work with the hydrogen electrode, Denham and Allmand * were led to infer the existence in aqueous solution of monovalent lead ions ($Pb^{\cdot}$), and Denham † adduced later further evidence from a "circulation" experiment. In this research a third method was adopted, viz. anodic solution. Various solutions were electrolysed by means of an anode of pure lead, and the loss in weight of the anode compared with the quantity of electricity used in the electrolysis.

Theory of Anodic Solution.—To see the possibilities of the method as well as to obtain a hint as to the most suitable experimental conditions (electrolyte, current density, concentrations), one needs a short account of the theory of anodic solution so far as it bears on lead.

N.B.—It is known that lead can be dissolved anodically as tetravalent ions ($Pb^{\cdots\cdot}$) in H_2SO_4 ‡ and in H_3PO_4, § but the discussion is here limited to the case of mono- and di-valent ion-production.

At a lead anode there are three processes possible :—

$$1.\ Pb + \oplus = Pb^{\cdot}$$
$$2.\ Pb + 2\oplus = Pb^{\cdot\cdot}$$
$$3.\ Pb^{\cdot} + \oplus = Pb^{\cdot\cdot} \parallel$$

Now if we *assume* that the equilibrium equation for lead is similar to that for copper,¶ the anodic processes may be summed up in accordance with the mass-action principle thus :—

$$2Pb^{\cdot} \rightleftarrows Pb^{\cdot\cdot} + Pb,$$

or, since the amount of Pb is practically constant—

$$K = \frac{[Pb^{\cdot\cdot}]}{[Pb^{\cdot}]^2}.$$

The *smaller* the current the closer will this equilibrium condition be realized in the electrolytic layer immediately surrounding the anode.** Besides the current, diffusion from this layer prevents an equilibrium state being realized.

Now if $Pb^{\cdot\cdot}$ and $Pb^{\cdot}$ diffuse away at different rates, then the amounts of $Pb^{\cdot\cdot}$ and $Pb^{\cdot}$ formed will so alter that K is kept constant (or rather tends to be).

It is clear, then, that if $Pb^{\cdot}$ can exist at all in an aqueous solution, they will be produced whenever an anode of lead is used to electrolyse that solu-

* *J.C.S.*, 93, 424 (1908).
† Loc. cit., 833 (1908).
‡ Elbs and Fischer, *Z. f. Elektr.*, 7, 343.
§ Fischer, loc. cit., 8, 398.
‖ And perhaps, like Hg, $2Pb + 2\oplus = Pb_2^{\cdot\cdot}$.
¶ Cf. Donnan in Abegg, *Kupfer*, iii. 2, 477–82.
** Cf. Dushman, *J. phys. Chem.*, 14, 385, for equilibrium relations in this layer.

tion. But it is also clear that the total amount of $Pb^{\cdot}$ formed ought to increase if we get rid of $Pb^{\cdot}$ more completely than $Pb^{\cdot\cdot}$. The question is, How can $Pb^{\cdot}$ be so got rid of?

Suppose we electrolyse a solution which will form complexes with $Pb^{\cdot}$ more completely than with $Pb^{\cdot\cdot}$, then the more completely the $Pb^{\cdot}$ are thus got rid of, the more will be formed relative to the $Pb^{\cdot\cdot}$. Now in the case of copper this is found to be the case when KCN is electrolysed with Cu anodes. If, then, lead is like copper in this respect, then by using as electrolytes solutions which form complex lead salts, there is the possibility that all or some of them will absorb $Pb^{\cdot}$ more completely than $Pb^{\cdot\cdot}$, and $Pb^{\cdot}$ will thus be produced at the anode in larger quantities.

So it was that in this research those solutions were used as electrolytes that were either known to yield, or were suspected of yielding, complex ions with $Pb^{\cdot\cdot}$, and hence might yield complex ions with $Pb^{\cdot}$ with more completeness.

The electrolytes used were *highly concentrated*, so that the ions should have full opportunity to form complexes.

Method of Work.—A bar of cleaned pure lead was first weighed, then used as anode in the electrolysis of the particular solution, and then again cleaned and weighed. If the anode is of pure metal the total loss of weight can be due to three possible causes :—

1. Chemical solution of lead in electrolyte.
2. Mechanical abrasion of lead during process of cleaning.
3. Electrolytic solution of lead.

To obtain, therefore, the amount of lead dissolved *electrolytically* we must first allow for the amount dissolved *chemically* and the amount detached *mechanically*.

In these experiments the following procedure was adopted :—

1. The amount of lead dissolved chemically was estimated by the use of a "blank" anode, i.e. another bar of pure lead of as nearly as possible the same length, breadth, and thickness as the real anode. Anode and blank dipped to the same depth in the electrolyte. They were placed as near as possible together (not so close, however, that the blank acted as part of a bipolar electrode). To ensure that blank and anode should be in a liquid of as nearly as possible the same composition the electrolyte was stirred by a stream of pure hydrogen. Surface oxidation of the lead was thus also reduced to a minimum. Under these conditions it was assumed that the amount of lead that the anode lost *chemically* was equal to the loss sustained by the blank.

The difficulty here is in regard to the surface of anode and blank. At the beginning of the experiment both surfaces would be equally bright, yet changes in brightness occurred often in one or the other, due to slight deposits (see under various electrolytes). Of course if the surface is not quite the same the chemical solution cannot proceed at the same rate, and the influence of this disturbing factor must be borne in mind.

The chemical solution cannot be neglected, as in many cases it is considerable (e.g. in $PbAc_2$ and H_2SiF_6), and even in KBr, KHT, and $Na_2S_2O_3$ it is appreciable.

2. That lead might be mechanically detached in cleaning was taken account of thus :—

(*a*) The anode and blank after electrolysis were both placed in pure water for a few minutes, then both cleaned with a smooth camel-hair brush, and finally both washed with water, alcohol, and ether, and then weighed.

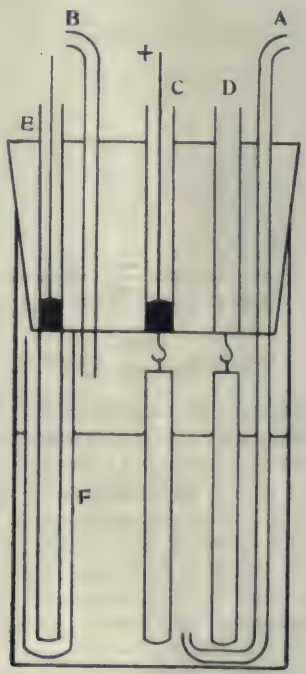
(*b*) Now suppose that in cleaning a certain amount of lead is mechanically detached by the brush. If we continue the experiment for *twice* the time

and then clean, we ought to detach about as much lead as before under the same brushing and not *twice* as much.

Suppose, however, we found that in the second experiment *twice* as much had been lost as in the first case, we should feel justified in attributing this extra anodic loss (i.e. the loss beyond that due to lead dissolving as $Pb^{\cdot\cdot}$ simply) not to mechanical detachment of lead by the brush, but to extra electrolytic solution, e.g. to the lead dissolving as $Pb^{\cdot}$ as well as $Pb^{\cdot\cdot}$, the amount formed depending on the length of the experiment. Of course, in any one experiment the extra loss might be compounded out of both factors, but by comparing such "time experiments" it ought to be possible to say whether the loss observed is *only* "mechanical" or whether extra electrolytic solution is also taking place.

The amount of lead which ought to have gone into solution if only $Pb^{\cdot\cdot}$ were formed was calculated by means of a silver coulometer in the circuit.

Apparatus.—The figure shows the form of vessel used in the electrolysis.



(I owe this sketch to the kindness of R. J. Plenderleith, Esq.)

Description.—A and B are the ingress and egress tubes for the pure hydrogen. C the anode, D the blank, are, as shown, attached to platinum hooks. The cathode of lead, fastened into its glass tube with cement to give it rigidity, was surrounded by a Karl Schleicher "Diffusionshülse F" to keep anodic and cathodic liquors separate. Three of these vessels were put in a row with a wash-bottle of pure water between each, and corresponding to each beaker was a silver coulometer, so that each vessel with its coulometer could be withdrawn at different times, the end beaker after Time I, i.e. when about 0·12 gr. of Ag had been deposited, the next beaker after twice as long, and the third after three times as long. (Times II and III, and so on for other times.)

The anode and blank were made from Kahlbaum's purest chemical lead (containing "1 part of impurity per 10,000" or 0·01 per cent.). This lead, supplied in short sticks, was rolled and cut to size with a penknife. Both were then 2 mm. thick, 8 mm. broad, and dipped into the electrolyte to about 48 mm. Of course more of the surface came into play as the hydrogen (impinging equally on anode and blank) splashed the liquid up higher. By using the anode and blank often as blank and anode, an attempt was made to keep the surface areas, which gradually diminish with the electrolyses, of as nearly as possible the same size.

With these dimensions we have the following current densities (Δ) corresponding to various currents in the circuit (ma. = milliamperes).

Ma. in circuit ...	...	...	100	50	30	25	20	10
$\frac{\Delta}{\text{cm.}^2}$ at anode	...	...	10·25	5·12	3·07	2·61	2·05	1·02

The experimental results were worked up as follows :—

ELECTROLYTE SODIUM ACETATE.

Current 25 ma.

Total anodic loss	...	...	...	0·4736 gr.	(I.)
Blank lost	...	...	...	0·0004 gr.	
∴ loss due to electrolysis		...	...	0·4732 gr.	
Ag deposit in coulometer		...	...	0·4874 gr.	
Or recalculated as $Pb^{\cdot\cdot}$ ...		...	...	0·4679 gr.	(II.)

For the sake of comparison, the amount of lead dissolved anodically is referred to 1,000 gr. of divalent lead. Thus :—

$$0{\cdot}4732 \times \frac{1{,}000}{0{\cdot}4679} = 1{,}011.$$

1,011 would therefore be the number corresponding to this experiment in the tables to follow. If it had been 1,000, of course it would have meant that in the experiment the lead had dissolved as divalent ions only.

Electrolytes.—As electrolytes were used, lead acetate, sodium acetate, potassium hydrogen tartrate, hydrofluorsilicic acid, potassium bromide, and sodium thiosulphate. The solutions were made in water which had been boiled and cooled while a stream of hydrogen bubbled through.

Experimental Results.—For the sake of clearness practically all the results obtained are here reproduced. In regard to their somewhat diverging character two facts must be borne in mind :—

1. In some of the solutions used more than half the "extra anodic loss" (p. 81) is contributed by the chemical solution. Now as the chemical solution of the blank is not likely (see above) to be *exactly* the same as that of the anode, when the chemical solution is large, one must expect divergencies.

2. If $Pb^{\cdot}$ is formed as well as $Pb^{\cdot\cdot}$, the amount of each formed will depend on the concentration of each, already in the layer immediately surrounding the electrode. Now stirring by the hydrogen stream during several hours (up to 6 hours) cannot be uniform, hence concentration relations must alter and hence divergencies must occur in final results.

A. LEAD ACETATE.

In using lead acetate we apparently start with an electrolyte containing a large number of $Pb^{\cdot\cdot}$ already, and hence might expect to get more $Pb^{\cdot}$ pro-

duced to keep K in equilibrium equation, constant (cf. Cu in $CuCl_2$ in Dushman's experiments), but Kahlenberg,* Conrad, etc., have shown that the concentration of $Pb^{\cdot\cdot}$ in lead acetate is very small (10^{-2} to 10^{-3} in N. $PbAc_2$) and Pick and Ahrens † attribute this to the formation of complexes. Hence the possibility that $Pb^{\cdot}$ might form complexes more completely than $Pb^{\cdot\cdot}$ (as above).

$PbAc_2$ (70 gr. to 1 l.).

Current 50 ma.

Times—I.	II.
1,011	1,002
1,007	999
996	
1,005	
Mean ... 1,005	1,001

The deviations in results are due to large chemical solution of lead in lead acetate solutions. Now if the lead is dissolving as $Pb^{\cdot}$ as well as $Pb^{\cdot\cdot}$, we should expect that the same mean would result from the experiments under Time II as under Time I : but if the lead is dissolving merely as $Pb^{\cdot\cdot}$, then the first mean ought to fall from 1,005 to 1,002·5. The fact that 1,001 was actually found shows that the lead dissolves in lead acetate under the conditions of the experiment as $Pb^{\cdot\cdot}$ only.

B. Sodium Acetate.

Here we start with an electrolyte containing $C_2H_3O_2'$ and no $Pb^{\cdot\cdot}$. Two series of experiments we carried out with solutions containing 350 gr. of the salt to a litre.

Series I.

In this series the anode was brushed after every experiment, as is the case with the other solutions used :—

Current in ma.	Times—I.	II.	III.	IV.	V.	VI.
100		1,007, 992 } 1,000		908, 1,006 } 1,002		
50		1,014, 1,012 } 1,013	1,018	1,004	1,005	
25	1,026, 1,024 } 1,025	1,019, 1,020, 1,027, 1,018 } 1,021	1,022, 1,036, 1,031 } 1,030	1,015, 1,011 } 1,013	1,012	1,010
12·5	1,025	1,019, 1,010 } 1,015	1,010			

* *Zeit. physikal. Chem.*, 17, 577. † Abegg, *Blei*, pp. 734–6.

Current in ma.	Means.
100	1,001
50	1,010
25	1,019
12·5	1,017
Mean	1,015

During the electrolysis lead acetate is formed. This tends to collect on the bright surface of the blank, so that it not only makes it heavier than it otherwise would be, but it also influences the chemical solution of the lead. This lead acetate also collects on the upper part of the anode, making the anodic loss less than it really is. To try to equalize matters, a second series of experiments was carried out. In these, the blank was well brushed, but the anode was merely washed and not brushed.

Series II.

Current in ma.	Times—I.	II.	III.
50	1,015 1,010 1,007 1,019 1,013	1,010 1,010 1,010	1,009 1,010 1,010
25	1,010 1,014 1,012	1,007 1,012 1,021 1,014 1,019 1,015	1,011 1,018 1,017 1,015
12·5	1,013 1,010 1,012	1,004 1,012 1,008	1,004 1,010 1,012 1,009

Current in ma.	Means.
50	1,011
25	1,014
12·5	1,010
Mean	1,012

For currents between 50 and 12·5 ma. we therefore obtain as means—

Series I	1,015	Mean ...	1,014.
Series II	1,012		

There appears therefore to be a real extra loss of lead greater than one would expect if all the lead went into solution as $Pb^{\cdot\cdot}$.

C. Potassium Hydrogen Tartrate.

Lead tartrate dissolves in excess of tartrate, forming complexes. Kahlenberg* and Hillger have shown that the concentration of $Pb^{\cdot\cdot}$ is then very small (c. 10^{-7}).

350 gr. were dissolved to 1 litre. High current densities cannot be used, as gas is then evolved at the anode (even at 100—25 ma. with the above dimensions of anode). Moreover, even at 12—10 ma. with a vigorous current of hydrogen, the anode gets coated with white deposits which are not always completely removable with the brush. The blank, however, remains bright, the deposit on the anode causing the divergencies in results. Thus :—

Current in ma.	Times—I.	II.	
12—10	1,016	998	966
	981	1,007	1,010
	1,002	1,004	1,008

The results show no evidence for other than $Pb^{\cdot\cdot}$ production.

D. Hydrofluorsilicic Acid.

H_2SiF_6 is not known to form complexes with $Pb^{\cdot\cdot}$, but when lead is purified by precipitating it cathodically from H_2SiF_6 solutions, the deposit is always of a very *smooth* character. Now smooth cathodic deposits are often due to the formation in electrolysis of intermediate complexes. Hence there is the possibility of complex formation in the case of H_2SiF_6.†

Moreover, observers had noted that a greater amount of lead dissolves at the anode in this electrolysis than corresponds to Faraday's law for $Pb^{\cdot\cdot}$.

The H_2SiF_6 was prepared from sand and CaF_2 by heating with H_2SO_4 and passing the SiF_4 formed into water :—

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

The SiO_2 was removed by filtration and the filtrate diluted to required normality.

* Loc. cit.

† I owe this hint to Dr. Allmand (cf. Dannael, *Zeit. f. Elektr.*, 9, 763).

H_2SiF_6 (TIME II).

Current in ma.

Normality.	100.	50.	30.	25.	20.	10.
2N.		1,007 | 1,011 ⟩ 1,009	1,029 | 1,029 ⟩ 1,029		998 | 1,019 ⟩ 1,009	1,012
0·4N.		1,004 (977) 1,002 1,005 ⟩ 1,003		996 | 1,024 ⟩ 1,010		1,023 | 996 ⟩ 1,000
0·08N.	1,023 | 1,000 ⟩ 1,012	993 | 1,006 ⟩ 1,000		1,014 (956) ⟩ 1,014		999 (968) 1,010 1,005 ⟩ 996

The divergencies are due to the large chemical solution of lead, e.g. the blank in the 2N. solution at 30 ma. dissolved to the extent of 13 mg., while the difference between the net anodic loss and that calculated for $Pb^{\cdot\cdot}$ was only 7 mg. The series of time experiments in which the experiments lasted twice as long shows this is the cause of the deviations.

Time IV.

Normality.	50 ma.	100 ma.
2N.	1,005 | 997 ⟩ 1,001	1,003 | 997 ⟩ 1,000
0·4N.	992 | 1,000 | 1,004 ⟩ 1,000	1,006 | 998 ⟩ 1,002
0·08N.	1,003 | 998 | 999 ⟩ 1,000	1,024 | 1,024 ⟩ 1,024

Only in the case of the 0·08N. acid at 100 ma. is there still uncertainty: but another small series of time experiments dispels this.

0·08N. H_2SiF_6.

Times—I.	II.	III.
997 | 999 ⟩ 998	991 | 996 ⟩ 994	1,003 | 999 ⟩ 1,001

There is therefore no evidence that lead dissolves anodically in hydrofluorsilicic acid otherwise than as divalent ions.*

* After these experiments were completed it was found that Sens had come to the same conclusion, *Zeit. f. Elcktr.*, 11, 229.

E. Potassium Bromide.

$PbBr_2$ dissolves in excess of KBr to form various complexes.* As is the case with sodium acetate, lead bromide tends to precipitate on the blank and on the top of anode. The anode (apart from the top) is easily brushed clean, leaving a smooth, shining surface.

KBr (350 gr. in 1 l.).

Current.	Times—II.	IV.	VI.
100	1,003, 995 } 1,010, 1,007 } 1,004	1,013, 1,016, 1,015, 1,008, 1,001, 1,007 } 1,010	
50	1,010, 1,009 } 1,010	1,001, 1,006 } 1,004	1,003, 998 } 1,001
20	1,015, 1,019 } 1,017	997, 1,002 } 1,000	
10	1,013, 1,006, 1,009, 1,016 } 1,011		

Doubt still remains in the case of the experiments at 100 ma. Another small series resolves this :—

100 ma.

Times—II.	III.	IV.	V.	VI.	VII.
995, 1,020 } 1,008	987	1,004	978, 1,003 } 991	1,003	984

Lead dissolves anodically in KBr as divalent ions only under these experimental conditions.

F. Sodium Thiosulphate.

According to Abegg,† $Na_2S_2O_3$ yields complexes with $Pb^{\cdot\cdot}$. During the electrolysis of solutions containing 350 gr. to the litre, lead sulphide is deposited in the cathode compartment. When the anode is taken from the solution after electrolysis it looks clean, only somewhat blue coloured. But there is a dark deposit on the anode which is readily removed with the brush. Analysis of some 60 mg. of this black substance gave a lead content that varied between 67 and 87 per cent. When this black substance is removed there is found to be a considerable anodic loss, which remains pretty constant in the time experiments.

* Abegg, *Blei*, p. 662. † Ibid., p. 703.

100 ma.

Times—I.	II.		IV.
	A.	B.	
1,018		1,032	1,036
1,038	1,041	1,035	1,037
1,023			
1,030	1,038	1,031	
Mean ... 1,027	1,040	1,033	1,037

A = anode cleaned with penknife for next experiment.

B = anode *not* cleaned with penknife for next experiment, but blank used as anode alternately in each separate experiment.

50 ma.

Times—I.	II.		III.	IV.
	A.	B.		
1,029	1,026	1,015	1,028	1,017
1,034	1,036			1,024
	1,054	1,019	1,028	1,031
	1,051			1,022
Mean ... 1,032	1,042	1,017	1,028	1,024

25 ma.

Times—I.	II.	III.
1,018	1,015	1,013
	1,026	1,027
1,021	1,026	1,027
Mean ... 1,020	1,022	1,022

20 ma.

Time II.

A.	B.
1,052	1,026
(1,082)	1,026
1,035	1,008
1,042	1,033
Mean ... 1,043	1,023

Means.

Series.	Mean.
100 ma.	1,033
50 ma.	1,030
25 ma.	1,021
20 ma.	1,033
Mean	1,029

In these experiments the blank remains perfectly clean and bright.

There is no doubt, therefore, that the anode loses considerably more lead than is accounted for by the causes mentioned on p. 80.

Results.

We have, then, as the results of this study of the anodic solution of lead :—

1. By electrolysing six solutions $PbAc_2$, NaAc, KHT, H_2SiF_6, KBr, $Na_2S_2O_3$ at various current densities, it has been shown that an anode of pure lead loses in general more lead than one would expect from Faraday's law for divalent ions.

2. It has, however, been shown, by using a blank electrode and by means of time experiments, that in the case of four solutions, viz. $PbAc_2$, KHT, H_2SiF_6, KBr, this extra loss is due to chemical solution and mechanical detachment in cleaning, and not to the lead dissolving as monovalent ions.

3. In the case of NaAc and $Na_2S_2O_3$ (particularly the latter), such an explanation was not readily applicable. It is true that the present research can be looked upon merely as preparatory to a more detailed study of these two solutions ; but so far as the suppositions underlying this work and its methods are sound, some further evidence may be adduced from these experiments for the existence of monovalent lead ions in aqueous solution. Should this be correct, the percentage amounts of $Pb^{\cdot}$ formed would be as follows :—

Sodium acetate	2·8 per cent.
Sodium thiosulphate	5·6 per cent.*

This investigation was carried out at the suggestion of Professor F. G. Donnan, F.R.S. I am grateful to him also for his interest and help before he left Liverpool. I wish also to thank Dr. A. J. Allmand, of this Laboratory, for expert advice.

Note added at the reading of the Paper.

The black deposit on the anode in the case of the sodium thiosulphate may be (1) a mono lead compound ; (2) possibly lead sulphide ; (3) finely divided lead due either (*a*) to breaking up of a mono compound depositing lead (cf. similar deposits in Denham's circulation experiment in cold arm of the tube), or (*b*) to peculiar nature of the electric corroding, whereby the

* For calculation see Donnan's *Kupfer*.

lead dissolved only in particular directions. This I do not think probable, owing to the fine nature of the deposit and its homogeneous character. I hope soon to continue the investigation on the thiosulphate, to try to bring the work to a more definite conclusion. Should I do so, I shall communicate the results to the Society.

Muspratt Laboratory of Physical and Electro Chemistry,
University of Liverpool.

THE VAPOUR PRESSURES AND SPECIFIC VOLUMES OF BINARY MIXTURES OF VOLATILE WITH NON-VOLATILE LIQUIDS.

By F. H. CAMPBELL, M.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

A number of attempts to arrive at a theory of the molecular state of binary mixtures of non-electrolytes has been made in recent years. Dolazalek*, for example, bases a far-reaching hypothesis upon vapour pressure measurements. Like the great majority of investigators in this field Dolazalek confined his attention to mixtures of which both constituents were volatile. It is obvious that the simplest case is that of a mixture of two normal liquids, of which only one is measurably volatile at the temperature of experiment. Since hitherto no case of this kind had been examined, the work, an account of which is given in this paper, was undertaken, in the hope that the results might throw some light upon the questions at issue between Dolazalek† and van Laar.‡ The former holds that the form of a vapour pressure curve of a binary mixture is dependent mainly upon chemical changes, while van Laar considers that all but exceptional cases can be explained by the physical action of the molecules upon one another. The want of data bearing upon cases of the kind mentioned is, no doubt, due to the smallness of the number of normal non-volatile liquids. A probable explanation of the smallness of the number of pairs of liquids of this type, including those in which one or both are associated, hitherto examined, is that no simple and accurate method was available for the purpose. The author has described such a method,§ and has applied it to the examination of a number of mixtures.

The pairs of liquids were as follows :—

Both normal—Oleic acid and ether.
Oleic acid and carbon disulphide.
Aniline and ether.

A normal non-volatile with an associated volatile liquid—Oleic acid and acetone.

An associated non-volatile with a normal volatile liquid—Sulphuric acid and ether.

Both associated—Glycerol and methyl alcohol.
Glycerol and water.

* *Zeit. Phys. Chem.*, 1908, 64, 727; 1910, 71, 191; 1913, 83, 40. And with Schulze (ibid., 1913, 83, 451).
† Loc. cit.
‡ Ibid., 1910, 72, 723; 1913, 83, 599.
§ *Trans. Farad. Soc.*, 1915

In the last case the values plotted are those recorded by Perman and Price.*

It will be seen that all possible types of mixture have been examined; the results recorded are, in general, consistent with Dolazalek's theory, that in cases in which the experimental results differ from those calculated from the mixture law, the reason is the formation of a dissociable complex, the breaking down of molecular aggregates, or both together. Thus the vapour pressure curve of a mixture of normal liquids will fall below the diagonal if solvate formation occurs; in absence of this tendency the curve of a mixture containing an associated liquid will lie entirely above the diagonal. According to van Laar, the assumption of solvate formation is entirely superfluous, for the vapour pressure curve of a mixture of normal liquids cannot be a straight line unless the critical pressures of the two liquids are equal; if they are not, the curve must lie above the diagonal, except when a compound is formed. His contention is not invalidated by the admission that the curve falls below the diagonal in such a case, since he makes it clear that he does not regard the form of the curve as a criterion, but insists upon other evidence, such as the isolation of the compound in the solid state. His calculations lead van Laar to the further conclusion that with associated liquids the curve must always fall below the diagonal. Although the results obtained by the author are explicable in a general way upon the solvate theory, it has not been found possible to get quantitative evidence in its favour. It would appear that the theory must undergo considerable modification before it is adequate to explain all known cases.

In most cases the specific volumes of a number of mixtures of each pair of liquids were determined. It was necessary to know these values in order to apply the correction referred to below; it was hoped, further, that the form of such curves might enable an independent calculation of the formula of the solvate, if any, to be made; as with the vapour pressure curves, it seems apparent that the assumption made by Dolazalek is too simple a one.

The vapour pressures of the pure liquids and mixtures employed were determined by measuring the rise of the mercury in an open manometer, caused by allowing a mixture of known composition to escape into a space previously filled with hydrogen.†

Determinations of densities were made in stoppered bottles, with graduated, capillary necks; the capacity of these bottles was 25 c.c.

The weight-compositions of the mixtures, given in the vapour pressure tables, are those determined by weighing, corrected for the amount of the volatile constituent which assumes the gaseous condition in the measuring apparatus, by means of the formula—

$$W_0 = W - \frac{273 \cdot pVM}{760 \times 22400\ T}$$

where W is the synthetic weight of the volatile component, W_0 the weight actually present in the liquid, V the volume of the gas, p its partial pressure, M its molecular weight, and T the absolute temperature. As the volume of the containing tube and the density of each mixture were known, the true proportions of each constituent could be calculated.

* *Trans. Farad. Soc.*, 1912, 8, 68. † Loc. cit.

Since the volume of gas did not exceed 12 c.c. in any case, and that of the liquid was 2·3 or 3·5 c.c., the correction was always small, the molar fraction of the volatile liquid being diminished by a few units in the third place.

Oleic Acid and Ether.—The oleic acid was a highly purified sample from Kahlbaum, it was almost colourless and odourless, but had a slight acid reaction, its density at 30°/4° was 0·8857, its vapour pressure was not measurable under the conditions of experiment. Although no direct proof appears to exist, oleic acid is taken to be normal, because it gives Traube's constant for normal liquids thus :—

$$\frac{282}{0{\cdot}898} - 287{\cdot}8 = 26{\cdot}2$$

a value in close agreement with the mean value given by Traube (25·9).*

It was found that a slight heat evolution occurs when oleic acid and ether are mixed, together with a diminution in volume.

In the tables which follow the symbols used are :—

N = the molar fraction of the volatile constituent,
D = the density,
V = the specific volume,
p = the observed pressure in millimetres, and
P = the ratio between p and the pressure of the pure volatile liquid determined under the same conditions.

It has been assumed that the values of P are practically the same as those which would be found *in vacuo*, an assumption shown to be justified in the case of the aniline-ether mixtures by the good agreement of the author's results with those obtained with the barometric method by Raoult.†

TABLE I.

Specific Volumes of Mixtures of Oleic Acid and Ether at 30·0° C.

Per cent. ether.	D.	V.	N.
0·00	0·8859	1·1291	0·000
9·52	0·8690	1·1509	0·286
24·55	0·8429	1·1863	0·554
40·91	0·8118	1·2317	0·725
53·29	0·7896	1·2664	0·813
100·00	0·7010	1·4265	1·000

Oleic Acid and Carbon Disulphide.—The admixture of these liquids is accompanied by a slight cooling and a very slight expansion. It was not possible to carry out a series of volume measurements owing to a shortage of oleic acid.

* *Zeit. Anorg. Chem.*, 8, 338, 1895, &c.
† *Zeit. Phys. Chem.*, 2, 363, 1888.

TABLE II.

Relative Vapour Pressures of Ether in contact with Oleic Acid at 30·0° C.

Per cent. ether.	*p*.	P.	N.
4·96	96·7	0·151	0·166
7·17	119·9	0·187	0·227
14·36	217·9	0·339	0·390
23·55	303·7	0·473	0·540
37·40	414·8	0·646	0·695
61·93	535·6	0·834	0·861
100·00	642·1	1·000	1·000

TABLE III.

Relative Vapour Pressures of Carbon Disulphide in contact with Oleic Acid at 30·0° C.

Per cent. carbon disulphide.	*p*.	P.	N.
3·12	40·9	0·095	0·107
15·75	164·0	0·380	0·409
25·85	233·7	0·541	0·563
34·77	290·5	0·673	0·664
40·51	316·3	0·732	0·716
56·14	366·6	0·849	0·827
100·00	431·9	1·000	1·000

Fig. 1 shows that both vapour pressure curves approach the diagonal very closely; this should indicate, according to van Laar, that the critical pressures of ether, carbon disulphide, and oleic acid are approximately equal. Such a deduction is not in accord with the facts, for, although that of oleic acid is unknown, different observers have found critical pressures for ether between 35·6 and 40·0 atmospheres, and between 72·8 and 78·1 atmospheres for carbon disulphide. Evidently the critical pressure of oleic acid cannot equal those of both ether and carbon disulphide; that it is equal to either is improbable.

Aniline and Ether.—This mixture was one of those examined by Raoult.* The author repeated the work because of the remarkable form of the curve obtained by plotting Raoult's results. In all mixtures in which the molar fraction of ether is less than 0·8 the curve lies above the diagonal, which it cuts at this point, the rest lies below it until the value for pure ether is reached. Both aniline and ether are normal, and considerable loss of energy accompanies their admixture. Fig. 2 shows that the author's observations confirm those of Raoult; it may be

* Loc. cit.

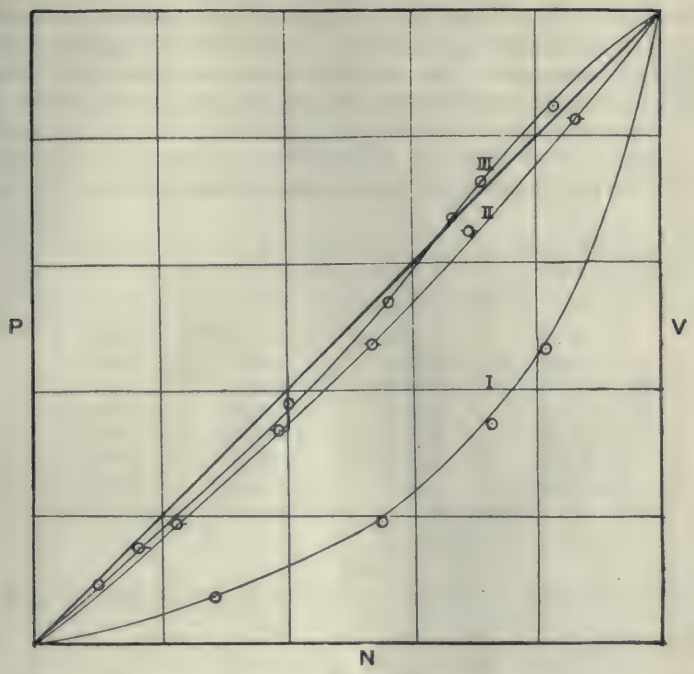


FIG. 1.

I. Specific volume curve of oleic acid-ether mixtures.
II. Vapour pressure curve of oleic acid-ether mixtures.
III. Vapour pressure curve of oleic acid-carbon disulphide mixtures

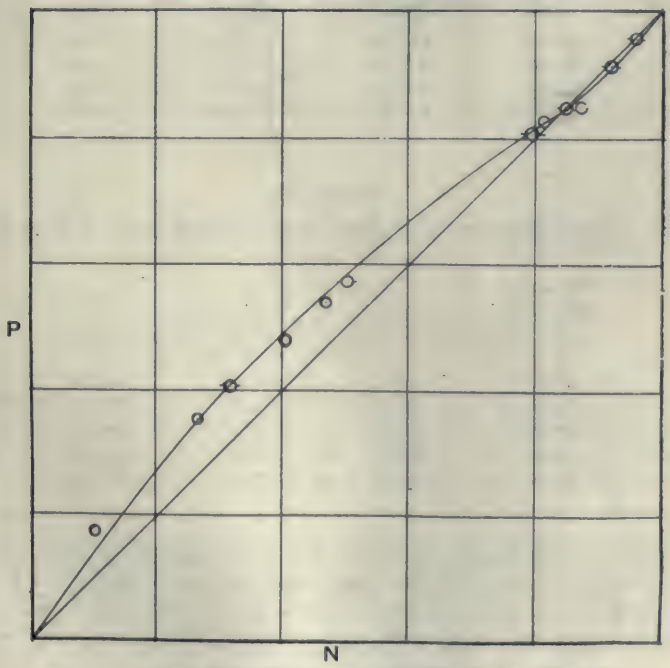


FIG. 2.—Vapour Pressure Curve of Aniline-Ether Mixtures.
⊙ Raoult's results; ⊙ author's results.

assumed that in the similar case of the nitrobenzene-ether mixtures the curve is of a somewhat similar form. These results appear to support van Laar's contention, but an observation of Linebarger* suggests another possible explanation, from the fact that the vapour pressure curves

TABLE IV.

Vapour Pressures of Aniline-Ether Mixtures at 20·0° C.

Per cent. ether.	p.	P.	N.
8·45	75·2	0·174	0·103
23·39	157·4	0·364	0·275
34·19	211·6	0·489	0·410
41·87	233·2	0·540	0·472
78·42	357·0	0·826	0·819
85·45	366·8	0·849	0·879
100·00	432·3	1·000	1·000

TABLE V.

Specific Volumes of Mixtures of Oleic Acid and Acetone at 30·0° C.

Per cent. acetone.	D.	V.	N.
0·00	0·8859	1·1291	0·000
2·82	0·8831	1·1323	0·123
20·44	0·8697	1·1499	0·555
37·39	0·8563	1·1678	0·744
59·94	0·8391	1·1916	0·879
100·00	0·8103	1·2340	1·000

TABLE VI.

Relative Vapour Pressures of Acetone in contact with Oleic Acid at 30·0° C.

Per cent. acetone.	p.	P.	N.
2·79	48·7	0·177	0·123
11·99	130·6	0·474	0·399
20·76	180·0	0·653	0·560
37·60	220·4	0·799	0·746
100·00	275·8	1·000	1·000

of pairs of normal liquids, of which one is but slightly volatile, lie above the diagonal. Unlike oleic acid, sulphuric acid and glycerol, both aniline and nitrobenzene are measurably volatile at the experimental temperatures employed ; it may be that solvates, also measurably volatile,

* *J. Am. Chem. Soc.*, 1895, 17, 615.

are formed. This hypothesis is put forward with reserve, but it has in its favour the facts that if it be made these cases no longer stand alone as exceptions, and that Linebarger found that, when mixed with carbon tetrachloride, the vapour pressure of nitrobenzine at 34·8° C. reached a maximum value of 6·3 mm. when its molar fraction was 0·49 and decreased with decreasing concentration of nitrobenzene. The vapour pressure of pure nitrobenzene at this temperature given by Linebarger is 1·16 mm.

The aniline used by the author was a pure sample from Schuchardt; twice redistilled, it boiled at a constant temperature, and had a density at 20°/4° of 1·0218. Its vapour pressure was not measurable under the conditions of experiment.

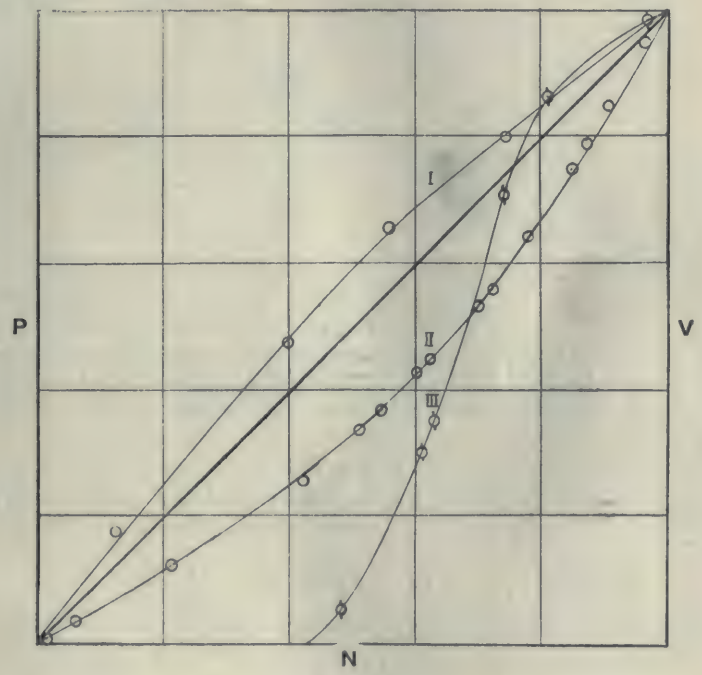


FIG. 3.

I. Vapour pressure curve of oleic acid-acetone mixtures.
II. Specific volume curve of sulphuric acid-ether mixtures.
III. Vapour pressure curve of sulphuric acid-ether mixtures.

Oleic Acid and Acetone.—The behaviour of this pair of liquids was studied in order to discover whether it supports the assumption that in the case of a pair of liquids, of which one is associated, the deviations from the law of mixtures will be such that the curve will lie above the diagonal. This was found to be the case. The specific volume curve is not plotted, because, as the table shows, it is practically a straight line.

Sulphuric Acid and Ether.—Pound* made an exhaustive study of the properties of mixtures of these liquids. He found the vapour pressure curve to be of a serpentine form, but as the acid used by him contained 5 per cent. of water, the work was repeated with anhydrous acid. The

* *J.C.S.*, 1911, 99, 698.

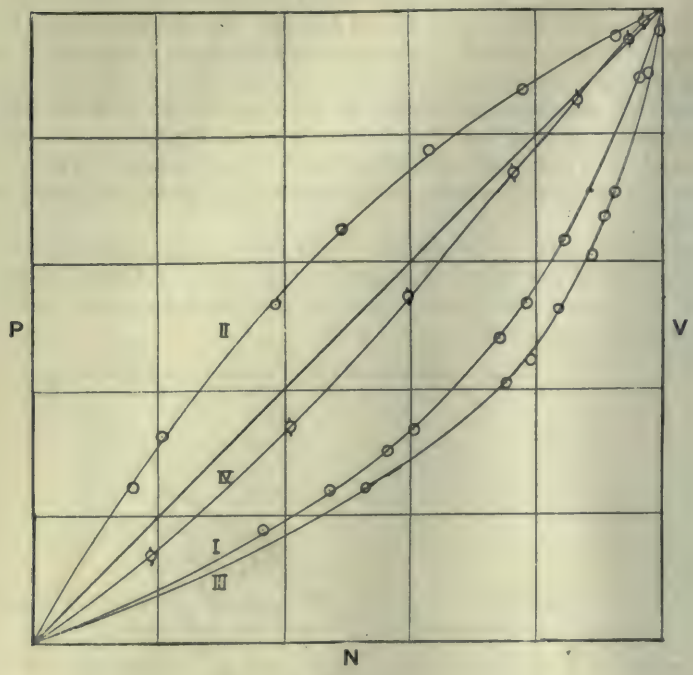


FIG. 4.

I. Specific volume curve of glycerol-methyl alcohol mixtures.
II. Vapour pressure curve of glycerol-methyl alcohol mixtures.
III. Specific volume curve of glycerol-water mixtures.
IV. Vapour pressure curve of glycerol-water mixtures.

TABLE VII.

Specific Volumes of Mixtures of Sulphuric Acid and Ether at 30·0° C.

Per cent. ether.	D.	V.	N.
0·00	1·8240	0·5482	0·000
1·37	1·7951	0·5571	0·018
5·02	1·7295	0·5782	0·065
17·47	1·5263	0·6552	0·219
35·42	1·2939	0·7729	0·421
44·77	1·1809	0·8468	0·518
48·01	1·14585	0·8727	0·550
53·98	1·08165	0·9245	0·608
56·16	1·0593	0·9440	0·629
64·12	0·9814	1·0189	0·703
67·12	0·9537	1·0408	0·730
73·30	0·8980	1·1136	0·784
81·87	0·8275	1·2084	0·857
84·65	0·8060	1·2407	0·880
89·00	0·7745	1·2911	0·916
96·375	0·7247	1·3799	0·972
100·00	0·7019	1·4247	1·000

values found are lower than Pound's, though the curve is of the same form. The differences are probably due to the fact that Pound used the barometric method, and took no special precautions to get rid of dissolved air. The acid used by the author contained a slight excess of sulphur trioxide, showing 100·3 per cent. H_2SO_4. It left 0·01 per cent. of residue, mainly ferric oxide. The specific volumes found are in good agreement with Pound's.

TABLE VIII.

Vapour Pressures of Ether in contact with Sulphuric Acid at 30·0° C.

Per cent. ether.	*p*.	P.	N.
41·59	34·8	0·054	0·485
54·51	192·2	0·299	0·613
56·35	229·7	0·358	0·631
68·76	455·1	0·709	0·745
76·90	554·4	0·863	0·815
97·13	631·8	0·984	0·978
100·00	642·1	1·000	1·000

The vapour pressure results point to the existence of a solvate with but slight tendency to dissociate. Its formula is probably $(C_2H_5)_2O \cdot H_2SO_4$. This compound possesses additive tendencies, and appears to be capable of taking up another molecule of ether.

Methyl Alcohol and Glycerol.—The glycerol used was a pure sample from Kitchen and Sons, further purified by distillation under reduced pressure. Its density at 25°/4° was 1·2578 ; it was without measurable vapour pressure. Heat is absorbed when glycerol and methyl alcohol are mixed, and a contraction takes place.

TABLE IX.

Specific Volumes of Mixtures of Glycerol and Methyl Alcohol at 56·0°C.

Per cent. methyl alcohol.	D.	V.	N.
0·00	1·2400	0·7812	0·000
2·96	1·2227	0·8189	0·079
9·72	1·1853	0·8437	0·236
16·76	1·1399	0·8772	0·366
23·89	1·1006	0·9086	0·474
31·02	1·0620	0·9416	0·564
34·99	1·0418	0·9599	0·607
50·61	0·9642	1·0371	0·747
56·22	0·9386	1·0653	0·787
66·17	0·8942	1·1183	0·849
90·40	0·7963	1·2558	0·964
100·00	0·7604	1·3151	1·000

TABLE X.

Vapour Pressures of Methyl Alcohol in contact with Glycerol at 40·0° C.

Per cent. methyl alcohol.	*p*.	P.	N.
6·26	62·1	0·241	0·162
8·55	83·8	0·326	0·211
18·33	137·5	0·533	0·392
25·53	167·1	0·648	0·496
38·28	199·6	0·774	0·634
56·27	222·9	0·864	0·785
83·68	244·8	0·949	0·937
100·00	257·4	1·000	1·000

TABLE XI.

Specific Volumes of Mixtures of Glycerol and Water at 56·0° C.

Per cent. water.	D.	V.	N.
0·00	1·2400	0·7812	0·000
4·36	1·2279	0·8144	0·189
17·65	1·1929	0·8383	0·523
37·92	1·1393	0·8777	0·757
42·81	1·1266	0·8879	0·792
50·27	1·1062	0·9040	0·838
60·00	1·0815	0·9246	0·884
66·54	1·0654	0·9386	0·910
70·51	1·0558	0·9471	0·924
89·99	1·0096	0·9905	0·979
97·05	0·9935	1·0065	0·994
100·00	0·9852	1·0150	1·000

TABLE XII.

Relative Vapour Pressures of Water in contact with Glycerol at 70·0° C.
(Perman and Price.)

p.	P.	N.
79·8	0·341	0·410
128·1	0·548	0·599
173·4	0·741	0·764
199·9	0·855	0·862
222·3	0·951	0·949
229·3	0·980	0·974
230·9	0·987	0·977
233·8	1·000	1·000

The vapour pressure curve is of the same form as is that of the oleic acid-acetone mixtures, hence it may be concluded that if a solvate is formed the effect is entirely masked by that of dissociation.

Water and Glycerol.—When these liquids are mixed a fair evolution of heat occurs; the contraction is, however, very small. There is little reason to doubt that glycerol forms at least one hydrate. The form of the vapour pressure curve is that to be expected where two opposing tendencies are operative, the curve lies below the diagonal when the quantities of water are relatively small, but lies above it when the molar fraction of the water is greater than 0·9, the dissociation of the water molecules being the main factor under these conditions.

Summary.

By the use of a new method, the effect of varying quantities of a liquid of negligible volatility upon the vapour pressure of volatile liquids dissolved in them has been determined.

It has been shown that the results receive adequate qualitative explanation, on the assumption that the form of vapour pressure curves is determined by molecular changes, accompanying the process of solution. Thus the solution may consist of a smaller number of particles than the liquids constituting it did before admixture, as the result of solvate formation; the number may be greater, owing to dissociation of an associated liquid. Probably the commonest case is that in which both solvate formation and dissociation occur together.

Attempts to apply Dolazalek's theory quantitatively were not successful, even in the simplest cases. It must be concluded that it requires amplification.

An explanation of the apparently abnormal behaviour of certain mixtures is put forward.

The specific volumes of a number of mixtures of pairs of liquid have been determined.

In conclusion, the author takes this opportunity of thanking Professor Masson. The work was undertaken at his suggestion, and he took every opportunity during its progress of securing its ultimate success by his interest and advice.

The School of Chemistry,
University of Melbourne.

DISCUSSION.

Professor A. W. Porter (*communicated*): Since for the binary mixtures considered by Mr. Campbell one of the components is non-volatile, the vapour pressure curve should be given by the same general formula as in the case of a solution of a salt in a volatile liquid, if allowance be made for any dissociation or polymerization which may take place. Now, in a paper read the same evening I have given a formula for such a case, viz.—

$$\log \frac{\pi_0}{\pi} = \frac{n}{N - an},$$

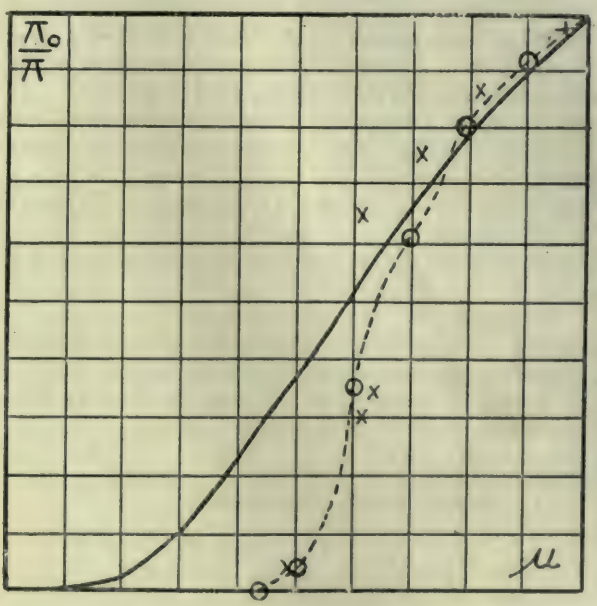
where n and N are the numbers of synthetic molecules of solute and solvent and a is a factor which may be interpreted as a hydration factor. If the salt dissociates (or polymerizes), this should be replaced by—

$$\log \frac{\pi_0}{\pi} = \frac{kn}{N - an},$$

where n and N are the number of synthetic molecules in the mixture, but each molecule of the solute consists of k molecules in the mixture. The value of k is greater than unity in the case of dissociation and less than unity in the case of polymerization of the solute. To compare with Mr. Campbell's experimental results, this requires to be expressed in terms of the molar fraction of the volatile component. This molar fraction is $\frac{N}{n+N}$; we will denote it by μ (Mr. Campbell's N). The equation now becomes—

$$\log \frac{\pi_0}{\pi} = \frac{K}{\frac{\mu}{1-\mu} - a}.$$

On the figure are plotted the values of $\frac{\pi}{\pi_0}$ against μ, (i) when $k = 1$, $a = 0$ (shown by a continuous curve); (ii) when $k = \frac{3}{4}$, $a = \frac{3}{4}$ (shown by a dotted



curve); (iii) Mr. Campbell's experimental values for sulphuric-acid-ether mixture (shown by crosses).

The interest of the last two arises from the similarity in their characteristics. It is not possible to obtain *exact* agreement except by taking k and a as variables. It is exceedingly plausible to assume that they really are variable. The value $k = \frac{3}{4}$ means that on the average 4 molecules of sulphuric acid aggregate into three molecules in the mixture; the value of $a = \frac{3}{4}$ means at the same time that each synthetic molecule of sulphuric

acid has $\frac{3}{4}$ molecule of ether associated with it, and therefore that each polymerized molecule of sulphuric acid has *one* molecule of ether associated with it.

The value of a is obtained, from the abscissa for which the vapour pressure vanishes, by means of the equation—

$$\frac{\mu}{1-\mu} = a.$$

There can be little doubt that this value is nearly right for the lower part of the curve. On the other hand, the curve cannot lie in any part above the straight-line diagonal unless polymerization of the non-volatile component is assumed. Now the region of the experimental curve which is found to lie above the diagonal is precisely that region (viz. μ nearly equal to 1) for which the validity of the theoretical curve given here can be claimed with the greatest confidence ; so there can also be little doubt of the existence of this polymerization.

THE ELASTIC STRENGTH OF METALS.

By FRANK CHARLES THOMPSON, M.Met., B.Sc.

(*A Paper read before the Faraday Society on Tuesday, May* 11, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

It has been recognized ever since the microscope was applied by Sorby to the study of metals that, normally, a pure metal consists of allotrimorphic crystals which meet along their boundaries. These latter would be expected at first sight to be surfaces of distinct weakness. It is a curious and rather unexpected fact, however, that when such a metal is broken in tension, fracture does not occur in the regions between the crystals but passes through the body of the crystal itself. In other words, the intercrystalline boundaries are by far the strongest part of the mass.

During recent years the idea that an amorphous intercrystalline layer occurs in normal metals between adjacent crystals has been put forward and developed by several authors, and in view of the mass of evidence which has been accumulated the theory may be accepted, at any rate as a working hypothesis. This theory is an extension of a more general one which has been developed in a long series of researches by Dr. Beilby, in which the production and continued existence of the vitreous amorphous state in plastically deformed metals has been experimentally demonstrated.

Glasses and other liquids in a drastically undercooled state are in general distinctly harder than the corresponding *crystalline* solid, and the remarkable strength of the intercrystalline boundaries has been explained, up to the present, simply by the fact that the "cement" which exists there is itself strong. Since, however, these intercrystalline films are of extreme thinness—certainly beyond the limit of microscopic vision—this explanation necessitates the assumption of a tensile strength for the cement of an order far beyond anything of which we have experience or are justified in assuming from our knowledge of other undercooled liquids.

The extreme practical and theoretical importance of an exact knowledge of the source of the strength of these junctions, however, renders it worth while to pursue the question further. Iron, which under normal conditions has a tensile strength of perhaps 20 tons per square inch, may, when the intercrystalline cement is impaired, become so brittle as to be broken even by hand.

Since the material filling the intercrystalline space is of the nature of an undercooled liquid, evidence of the normal properties of this state should be obtainable. In this connection viscosity effects have often been observed, and in particular for the present purpose surface tension phenomena may be expected. The conception that surface tension effects are to be observed in the amorphous layer of metals is not put forward here for the first time. The idea, which was originally due to Quincke, has been used by many authors. Dr. Beilby (1), whose writings are permeated with the idea, has definitely

shown that the forms assumed by the surface layers of metals during mechanical deformation or subsequent annealing are controlled by surface tension. Similar forces are also at work within the amorphous films formed on each plane of slip. Brillouin has used the hypothesis in order to explain the behaviour of metals in tensile tests, and the polyhedric form of the crystals of an annealed pure metal has been referred by P. Curie to surface tension in the crystal boundaries. Tammann (2) also has considered the relationship of the surface tension to the strength in connection with the crystalline structure of metals during crystallization from the liquid state or after having been cold-worked. A quantitative relationship has been derived by the same author. If f is the strength of a lamina at its recrystallization temperature after cold-rolling, wire-drawing, etc., n the number of gliding planes in it parallel to its surface, a_1 the tension in the gliding planes, which is always less than a, the surface tension in the free surfaces, then—

$$2na_1 + 2a = f.$$

Rosenhain and Ewen (3), referring to the reason for the retention of the intercrystalline metal in the amorphous condition, say, "The forces . . . may possibly be of the nature of capillarity." The theory, however, is used in the present Paper in a novel and more definite manner, and in addition a quantitative interpretation is adopted.

When two similar plates are separated by a film of a liquid which wets them, a marked attraction occurs. The intensity of the attraction is :—

$$\frac{2AT}{d} \text{ dynes,}$$

where—

A is the area of the plate wet by the liquid,
T is the surface tension of the liquid,

and—

d is the thickness of the film.

At the crystal boundaries in a metal not dissimilar conditions obtain. Two crystalline portions are separated by a film of "undercooled liquid." In this case, however, the pressure must be regarded as being derived not from that of the atmosphere, but from the vectorial forces of crystallization.

Such attractions may attain very considerable magnitudes, and the strength (elastic) of the junctions, and therefore also of the metal itself, is regarded as being due to these attractions between all the adjacent faces in the mass. An example of such adhesions is afforded when two blocks of ice are placed loosely together. As the excess water between the faces drains away, the remaining film draws the masses together with a force sufficient to weld them into one coherent whole. To the author this action appears analogous to the crystalline growth of a metal during annealing.

One of the most important explanations to be required from any theory of the source of the intercrystalline strength of metals is the mechanism by which the great strength of the junctions is obtained despite their extreme tenuity. As has already been shown, any explanation on the ground of the actual strength of the films themselves does not appear satisfactory. With the new theory, however, the difficulty ceases to exist. Since the attraction between the crystals is inversely proportional to the distance between them, the very thinness of the films is the source of their greatest strength, and if for any reason the width of these is increased the strength of the mass is lowered.

The greatly increased elastic strength of a fine-grained metal over a

coarser one depends, on the theory, simply on the increased area across which the attraction occurs, and thus on the greater resolved force in any direction.

Effects of Strain on Metals.

It now becomes of interest to discover to what extent such a theory is in accordance with the well-known facts relating to the effects of strain on metals, and in particular with the stress-strain diagram.

Fig. 1 shows the curve obtained by Robertson and Cook (4) following Dalby (5), which probably most accurately represents the phenomena. For strains below the elastic limit stress and strain are proportional. When this range of proportionality is passed, however, the curve bends abruptly downwards, reaches a minimum, after which it ascends again to the maximum

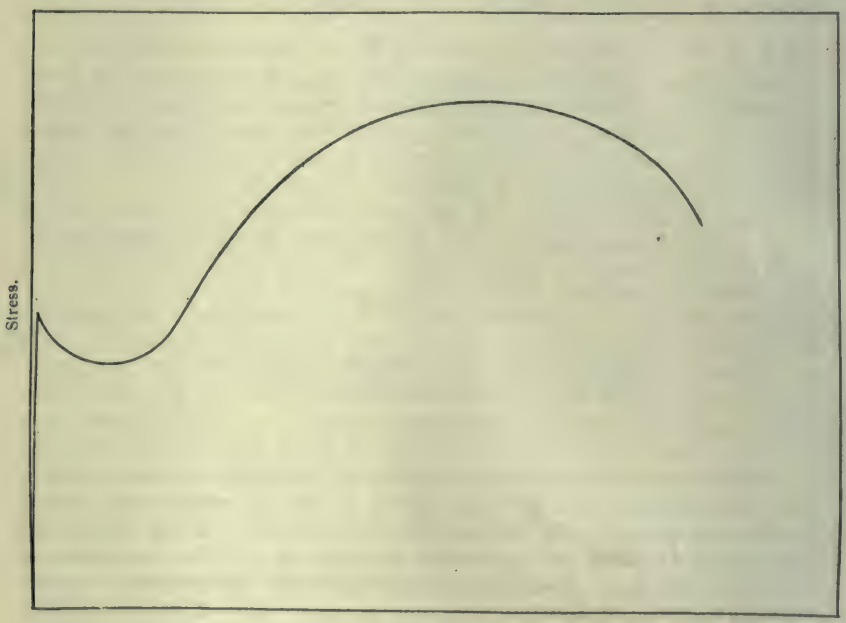


FIG. 1.

stress. It is in the marked dip at the "yield point" that the diagram differs essentially from those usually obtained.

On the present theory the elastic strength of a metal is the resultant in the direction of the application of the stress of the interface attractions. When the applied stress is less than this value comparatively little effect is produced and the strain will be small. The extension will be made up of the true elastic deformation of the crystalline matter itself and also of the slight separation of the crystals at their boundaries. Which of these factors will be the greater cannot be stated *a priori*. When the load is removed the extension disappears, although slight viscosity effects have been observed even within the elastic range. The true elastic deformation will be removed with great rapidity, but the rate at which the attractions will draw the crystals back to their original positions may conceivably be much less, as actual flow of the viscous amorphous material seems necessarily to accompany the

changes. When the increasing stress applied to the specimen becomes equal to the resultant of the attractions the elastic limit is reached. A further stress, exceeding the resistance of the interface attractions, draws the crystals apart and permanent set occurs. Actual separation of the crystals is prevented by the flow of amorphous metal from more highly compressed localities. This increased thickness of the amorphous film is of the greatest importance, since the intercrystalline attraction, i.e. the resistance of the metal to the stress, is inversely proportional to the thickness d. The effect, therefore, of the drawing apart of the crystals just beyond the elastic limit is to lower markedly the resistance to the stress applied. During this stage of the test every increase of load, by increasing the thickness of the films, produces a rapid fall in the resistance to the stress, and a period of instability—the yield point—occurs. The decided drop in the stress-strain curve when the elastic limit is passed is thus explained.

Up to this stage the demands of the theory seem to be in complete accord with experience, but much further it is impossible to go. Once the elastic limit is passed, slipping occurs on numbers of cleavage planes within each crystal. At each slip amorphous material is formed, across which further attractions, which cannot be allowed for, act. The metal is stiffened up and the curve rises again, but at an indeterminate rate.

Having seen how eminently satisfactory is the qualitative agreement between the demands of the theory and the experimentally determined diagram, it becomes of interest to determine what quantitative significance the formula possesses. At the outset two difficulties present themselves. In the first place the thickness d of the intercrystalline cement is not known, though it is probably nearly within the range of microscopic vision. The second source of uncertainty arises from the lack of knowledge of the surface tension of these films. It has been shown, however, that the surface tension of an undercooled liquid is quite unaffected by the freezing-point (6), the curve expressing the relationship of this quantity to the temperature being a straight line without inflection, till in the neighbourhood of the critical temperature the tension becomes zero. Thus, if the critical temperature and the surface tension of the molten metal at any definite temperature are known, the surface tension of the amorphous material at room temperatures can be calculated. The critical temperatures for practically all metals are unknown, but a rough approximation may be arrived at from the use of the formula of Thorpe and Rücker :—

$$\frac{D_t}{2T_c - T} = \frac{D_o}{2T_c - 273},$$

where—

D_t = density of liquid metal at temperature T°A,

D_o = " " " 273°A,

and—

T_c°A = critical temperature.

For purposes of calculation of the critical temperature D_o is taken as the density of the ordinary metal itself—if known in the work-hardened state—since changes of density when a metal is converted into the amorphous condition by cold work are not great. The values of the critical temperature arrived at in this way are certain to deviate markedly from the truth, but since the temperature is in all cases very high compared with that at which the surface tension of the molten metal has been determined—usually the freezing-point—the increase in the experimentally determined figure for

the surface tension will be slight, whence the latter will be known for the amorphous films within fairly narrow limits.

The total attraction per c.c. is according to the formula—

$$= \frac{2AT}{d},$$

where A is the total intercrystalline area per unit volume.

The resultant attraction therefore in any one direction is—

$$\tfrac{1}{3} \cdot \frac{2AT}{d}.$$

Now, considering the crystals as perfectly regular rhombic dodecahedra, and remembering that A is one-half of the total crystalline surface, the resultant in any direction, i.e. the elastic limit, will be $1{\cdot}25n\frac{T}{d}$, where n is the number of crystals per cm. Since, however, the crystals never are uniform dodecahedra, the area will be greater, and probably—

$$\text{E (the elastic limit)} = 1{\cdot}5n\frac{T}{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

expresses the attraction as nearly as it is possible to do so. The foregoing is by no means a rigid proof, but the equation appears to correspond with the experimental results with a reasonable degree of exactness.

For pure metals only has the surface tension been accurately determined, and these alone, therefore, are available for the experimental verification of the expression. The values of the surface tensions used are those given by Smith (7) with the exception of the values for cadmium, which is Quincke's, and for iron, which is not known at all well, and where 1,350 is taken as being as near as possible.

The values of the densities are taken from the tables of Landolt and Börnstein, supplemented where possible by the valuable determinations of Pascal and Journiaux (8).

Copper, zinc, antimony, silver, lead, tin, nickel, and very pure iron were selected for examination. All, with the exception of the nickel, were practically free from any impurity. The latter metal, however, contained 0·79 per cent. of manganese, the remains of 1·5 per cent. thermit manganese which had been added to the molten metal to remove oxygen taken up during melting. The copper, zinc, antimony, silver, lead, and tin were cast in bars 12 in. long and 1 in. diameter, from which the tensile test pieces were prepared with 2 in. turned accurately to a diameter of 0·564 in. The iron and nickel were cast as 2-in. square ingots and rolled to 1-in. round bars. To investigate the influence of alterations of crystal size in the same metal, test pieces were prepared of the iron, after several different thermal treatments, viz. :—

(1) As received from the rolls.
(2) Normalized, i.e. heated to 900° C. and cooled in air.
(3) Quenched from 900° C. and then tempered at 650° C.
(4) Heated to 900° C. and cooled over 12 hours.
(5) Heated to 900° C., kept at the temperature for about 15 hours, and cooled over another 40 hours.

By these treatments the number of crystals per cm. was varied from 690 in sample (3) to 10 in sample (5).

The analysis of the iron was :—

C.	Si.	Mn.	S.	P.	Al.	Fe (by difference).
·049	·04	·03	·02	·016	trace	99·87

Figs. 4–7 are micrographs taken at 100 diameters of the structure of 2, 3, 4, and 5.

The test pieces were broken on the 10-ton centre of a Buckton testing-machine. The elastic limit was determined in the cases of the silver, copper, nickel, and iron with the aid of a Metzger extensometer reading to ·0001 in. In the other tests it was somewhat less exactly determined as that stress at which permanent elongation could first be observed with dividers (i.e. an elongation of ·01 in. on a gauge length of 2 in. or 0·5 per cent.). The bars of zinc and antimony broke without any observed deformation, the elastic limits coinciding in these cases with the maximum stresses. Since annealed copper is practically without any true elastic range, great care was taken with the test of this metal in the cast state, and up to 1·52 tons per square inch perfect proportionality between stress and strain was observed. The elastic limit is taken as the limit of proportionality of stress and strain.

Table I records the experimental results.

TABLE I.

Material.	Elastic Limit. Tons per sq. in.	Max. Stress. Tons per sq. in.	Elongation per cent. on 2 in.
Copper	1·52	9·0	22·0
Zinc	2·64	2·64	0·0
Antimony	0·69	0·69	0·0
Nickel	11·5	36·71	66·4
Lead	0·60	0·98	54·5
Tin	1·20	2·40	36·5
Silver	1·40	8·0	60·0
Iron (annealed)	9·61	21·1	47·0
Iron (normalized) ...	12·0	21·8	47·5
Iron (quenched and tempered)	14·0	23·2	46·0

TABLE II.

Metal.	No. of Crystals per sq. cm. n.	T.	$1{\cdot}5nT$.	E.L. $\times 10^{-8}$ Dynes per sq. cm.
Lead	4·0	443	$2{\cdot}66 \times 10^3$	0·93
Antimony... ...	7·5	285	$3{\cdot}2 \times 10^3$	1·04
Tin	5·9	501	$4{\cdot}45 \times 10^3$	1·86
Silver	5·5	1,040	$8{\cdot}6 \times 10^3$	2·17
Copper	8·7	1,246	$1{\cdot}62 \times 10^4$	2·35
Zinc	15·7	726	$1{\cdot}72 \times 10^4$	4·08
Nickel	256	1,350	$5{\cdot}2 \times 10^5$	17·8
Iron (annealed) ...	276	1,350	$5{\cdot}6 \times 10^5$	14·8
Iron (normalized)	343	1,350	$6{\cdot}9 \times 10^5$	18·6
Iron (quenched and tempered)	690	1,350	$13{\cdot}9 \times 10^5$	21·6

In Table II the number of crystals per cm.n, the calculated surface tension of the amorphous film (T), $1{\cdot}5nT$ and the elastic limit E in dynes per sq. cm. are recorded. With the exception of a slight alteration in the position of the nickel—readily explicable since it alone deviates appreciably from absolute purity—the orders of the metals in the last two columns are identical, and it is impossible to believe that such agreement could be found did not the theory of the elastic strength of metals at present under consideration contain distinct elements of truth.

The three tests made on the pure iron give rise to a point of considerable interest. In a ductile metal such as this, it has been conclusively proved that fracture in tension occurs within the crystals themselves and not in the intercrystalline boundaries. Now, there is no reason to suppose that the heat treatments applied would appreciably alter the state of the crystalline matter. Hence, beyond a certain small stiffening-up, due to the greater amount of the amorphous cement, one would not expect the maximum stresses in the three cases appreciably to differ. This is shown to be the case, since the increase in the maximum stress from least to greatest is only 10 per cent. On the

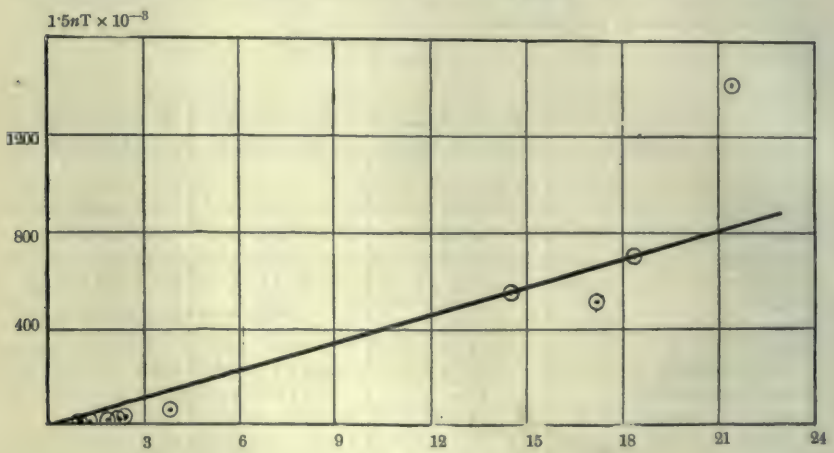


FIG. 2.—Elastic limit × 10^{-8} (dynes per sq. cm.).

other hand, according to the theory here advanced, the magnitude of the elastic limit is intimately connected with the boundaries between the crystals, and the change in this quantity in the cases under consideration is no less than 46 per cent. To the author this seems striking evidence that the conditions governing the elastic limit are, as his theory demands, essentially different from those governing the maximum stress.

Probably, however, the most striking proof of the truth of this is supplied by figures published by Professor Arnold (9) of tests made on a steel casting, as cast and after drastic annealing.

	Elastic Limits. Tons per sq. in.	Maximum Stress. Tons per sq. in.
As cast...	16	25·5
Annealed	4	24·3

In Fig. 2 the last two columns of Table II are plotted against each other, and it will be seen that to a first approximation, which is all that can be expected, the relationship is a linear one.

If—

$$E = 1{\cdot}5n\frac{T}{d},$$

then

$$\frac{1{\cdot}5nT}{E} = d,$$

the thickness of the amorphous intercrystalline film.

From Fig. 2 $d = 3{\cdot}7 \times 10^{-4}$ cm.

This value will be discussed later. There is, of course, no reason why the thickness of the film should not vary markedly from metal to metal, but the results of Table II and Fig. 2 suggest that in all the metals examined the thickness of the intercrystalline cement is of the same order.

During a consideration of the possibility of extending the application of the equation of Van der Waals to the solid state, Traube (10) arrived at the conclusion that the hardness of a metal is determined by its "intrinsic pressure." That this is not a complete expression of the facts is evident from the well-founded experience—confirmed by results on iron contained in the present Paper—that the hardness of a metal is largely determined by the size of the component crystals, increasing as these decrease. Thus, in any mathematical expression of the hardness of a metal a term, depending on the grain size, must be introduced. Such a term equation (1) does contain. For a single crystal it may well be that Traube's hypothesis holds, but such isolated crystals of metals are merely curiosities. As has been already noted, however, the maximum stress of a pure metal is dependent chiefly on the crystalline material itself, and only to a smaller extent on the crystal boundaries. Hence this measure of the hardness of a metal will probably bear an intimate relation to the intrinsic pressure.

In view of the close relationship between the surface tension and intrinsic pressure of a substance, it is to be expected that, if the author's theory is true, a certain degree of proportionality will be found between the elastic strength of a metal and its intrinsic pressure.

TABLE III.

Metal.	Intrinsic Pressure. Megabars.	Elastic Limit. Tons per sq. cm.	Max. Stress. Tons per sq. cm.	Brinell Hardness (500 kilos).
Lead ...	51,500	0·60	0·98	Too soft to measure
Tin... ...	73,100	1·20	2·40	Do. but harder than lead
Zinc ...	108,900	2·64	2·64	29·7
Antimony...	120,000	0·69	0·69	Crushed
Silver ...	161,900	1·40	8·00	—
Copper ...	236,100	1·52	9·00	45
Iron ...	323,900	9·61	21·1	70
		12·0	21·8	83
		14·0	22·2	105
Nickel ...	324,600	11·5	36·71	109

Table III gives for the metals used in the present research the intrinsic pressure (Traube's results), the elastic limit, maximum stress, and Brinell hardness. Though a certain correspondence between the intrinsic pressure and the elastic limit is evident, the agreement is far less perfect than when

the equation (1) is utilized. The maximum stress results checked by the Brinell hardness, however, strikingly confirm Traube's theory, with the exception of the values for antimony.

Two further details pointing in the same direction may here be noted. Hanriot (11) has recently shown that a cube of metal subjected on every face to considerable hydraulic pressure was appreciably hardened, although no distortion of the crystals could be detected microscopically. Cleavage slipping, therefore, presumably did not occur, so that the hardening was not due to an increase in the quantity of the amorphous modification. The result admits of a simple explanation in view of the theory under consideration. Pressure from all sides would tend to produce closer contact between adjacent crystals, so that d in equation (1) would be decreased and E in proportion increased.

The second point arises from the discovery of Schottky (12) that the strength of gold leaf begins to decrease when the thickness is reduced below a certain value. The extra reduction would produce, if possible, more amorphous material than before, and so should, according to present conceptions, give a still harder material. Such a result, however, would follow necessarily from the surface-tension theory of strength. As the amount of the amorphous variety increases, more and more surfaces over which the attractions could be exerted would at first be formed, and hence an increase of strength result. After a very great amount of cold work has been put upon the metal, the crystalline phase will have decreased to such an extent, however, that the area across which attraction occurs will have decreased also, and a corresponding loss of strength occurs.

Effect of Temperature on the Mechanical Properties of Metals.

As has already been emphasized, the normal fracture of a ductile metal at room temperatures passes through the body of the crystals. At the same time the crystals are pulled out, and slipping along cleavage planes occurs. Above a certain temperature, however—720° C. in the case of copper—the fracture changes entirely in type, and now passes through the intercrystalline regions. The crystalline matter is not appreciably deformed, the metal having become typically brittle. This remarkable change is the result of the gradual loss of strength of the intercrystalline junctions. So long as these are stronger than the crystals, so long is the low-temperature type of fracture found. When the conditions are reversed, intergranular weakness results, and the fracture passes between the crystals.

This loss of strength of the cement has been explained in a perfectly satisfactory manner (13) by the reversion of the extremely viscous undercooled liquid to a more mobile—and hence weaker—state. The present hypothesis, however, still affords a simple and rational explanation of these facts. The surface tension falls off as the temperature rises, the crystals grow in size at the same time, i.e. n in equation (1) decreases, and Van der Waals has shown that surface films may increase in thickness as the temperature is raised, i.e. d increases. Thus every term in the equation—

$$E = 1{\cdot}5n\frac{T}{d}$$

changes so as to reduce the value of the elastic limit. When the crystalline part has become stronger than the junctions, the stress sufficient to overcome these will be sufficient to smash the specimen. Hence the maximum stress coincides with the elastic limit. Since $1{\cdot}5n\frac{T}{d}$ is a measure of the strength of

the crystal junctions, it represents above the temperature at which the order of the relative strengths of these and the crystals changes the maximum stress. Below that temperature it is a measure of the elastic limit, thus in the curve tensile-strength–temperature an abrupt change should occur. This is in entire accord with the results obtained by Bengough and Hanson (14) with copper. Fig. 3 shows the typical curve which these investigators obtained. The interesting corollary arises from these considerations that the elastic-limit curve below the temperature of change should be a continuation of the maximum-stress curve above. The paper quoted does not contain the values of the elastic limits, but if the curve above P be continued back the value of the limit at room temperature for annealed copper broken in air is 3 tons per sq. in., and for hard-rolled copper 6 tons per sq. in., results of approximately the right order of magnitude.

For a pure metal, however, the curve will not be straight. When such a temperature is attained that the crystalline growth has an appreciable velocity, the term n of equation (1) starts to decrease rapidly, and with it the elastic

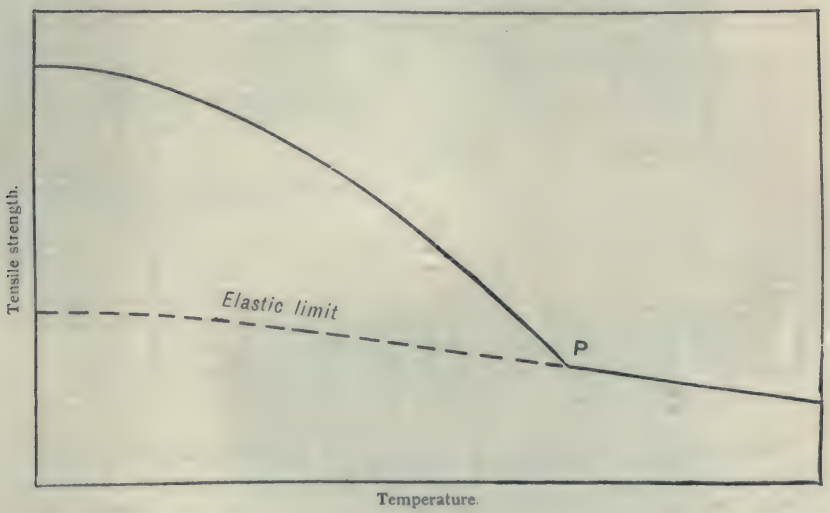


FIG. 3.

limit. This curve in the diagram will therefore bend downwards. The values of the elastic limit of copper just obtained by simple extrapolation will err notably on the high side. The curve showing the relationship of the elastic limit of copper to temperature has, however, been obtained by Huntington (15), and is exactly of this type.

Electrical Conductivity.

One calculation of the order of thickness of the intercrystalline medium has already been obtained, viz. $3{\cdot}7 \times 10^{4}$, and it is also possible to obtain the same value using determinations of the electrical resistivity.

When an electrical current is passed through a normal metal the opposed resistance may be considered as the sum of two factors, one for the actual crystalline material, the second depending on the resistance of the crystalline junctions. Since the actual thickness of these latter will always

be small, the length of the crystalline material to be traversed will remain sensibly constant, so that the crystalline factor will itself be a constant. The total resistance of the boundaries will depend on the number of these to be traversed, so that

$$\rho_1 = \rho_2 + nR \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)^*$$

where—

ρ_1 = specific resistance of the sample.
ρ_2 = specific resistance of the crystalline material.
n = number of crystals per cm.

and—

R = the boundary resistance.

For the experimental testing of this equation the samples of heat-treated iron were used. The specific resistances were measured by comparing the p.d. between the ends of the bars 8 in. long and 1 cm. diameter with that in a standard low resistance when traversed by the same current. The results are found in Table IV.

TABLE IV.

Treatment.	No. of Crystals per cm.	Sp. Resist. in microhms per c.c.		
		Observed.	Calculated.	Difference, Observed—Calculated.
Annealed drastically ...	?	7·152	—	—
Annealed	276	7·251	7·307	— ·056
Normalized	343	7·513	7·422	+ ·091
As received	426	7·563	7·564	— ·001
Quenched and tempered ...	690	7·986	8·019	— ·033

Without a single exception the increased size of grain is accompanied by a corresponding decrease in the specific resistance. To 1 per cent., which is as near as the mean crystal size can be determined, the equation (2) holds good.

The value 7·56 microhms per c.c. for the iron as received from the rolls is in excellent agreement with that (7·6) arrived at by Benedicks (16) from his study of the specific resistance of steels.

The number of crystals per cm. in the drastically annealed sample could not be determined, as the structure was most curiously and to the author in-

* Since writing this, the attention of the author has been drawn to a paper by von Weimarn (*International Journal of Metallography*, iii., 2, p. 65) in which a very similar relationship has been given. Reasoning from the known properties of colloidal solutions, it is found that the measured resistance of a metal ρ is the sum of two values ρv and ρs, of which the first depends of the volume of the sample, the second on the surface energy. Thus—

$$\rho = \rho v + \rho s.$$

In addition ρs is dependent on the number of crystal grains per cc.

The close relationship of this expression to the equation of the author will be readily seen. No attempt, however, was made to supply any experimental evidence in support of the idea.

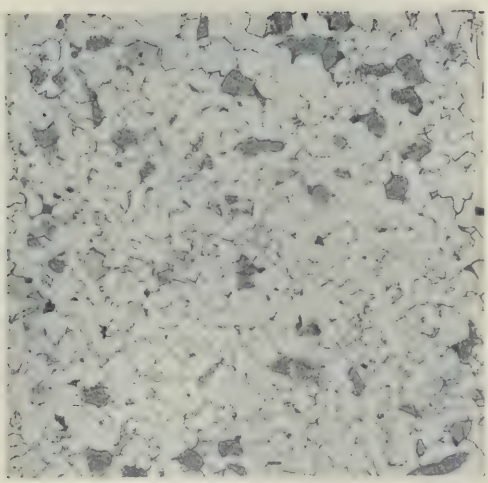


FIG. 4.

FIG. 5.

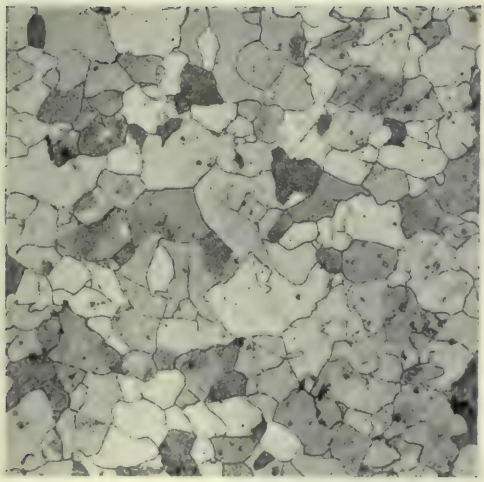


FIG. 6.

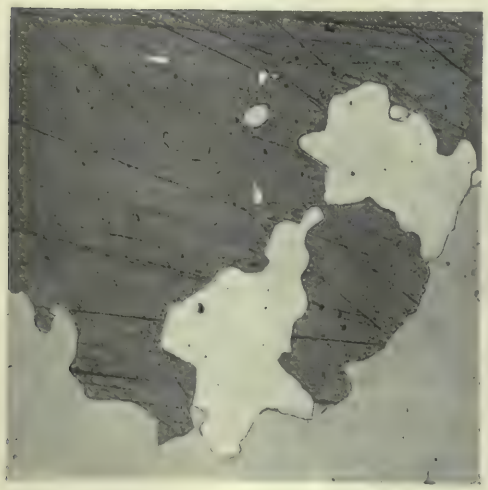


FIG. 7.

explicably uneven. About seven-eighths of the microsection consisted of crystals so large as to be visible to the naked eye, while the remainder consisted of crystals almost as fine as those in the annealed sample (Fig. 7).

From the values obtained the true specific resistance of the crystalline material ρ_2 and the boundary resistance R could be calculated. Substituting the mean values of these in equation (2) it becomes for iron—

$$R = 6{\cdot}83 + 1{\cdot}72n \times 10^3 \text{ microhms per c.c.}$$

The value 6·83 microhms per c.c. is the only logical value for the specific resistance of iron. The great variation in the specific resistance as the grain size alters (7·15–7·99) seems to explain the wide divergence of the values obtained by different investigators for this "constant," even where pure materials have been used. In view of these results no determination is complete which does not also give the crystal size and sufficient data for the calculation of ρ_2 and R.

If equations (1) and (2) are combined—

$$d = \frac{1{\cdot}5\,T}{E} \cdot \frac{\rho_1 - \rho_2}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from which, with the values already determined, d can be calculated.

Material.	d cm.
Annealed iron	$3{\cdot}4 \times 10^{-4}$
Normalized iron	$4{\cdot}3 \times 10^{-4}$
Quenched and tempered	$6{\cdot}3 \times 10^{-4}$
Mean	$4{\cdot}7 \times 10^{-4}$

This value is in very close agreement with that already obtained, $3{\cdot}7 \times 10^{-4}$ cm.

It is at once evident, however, when considering the result, that 4×10^{-4} cm. is an impossible figure for the thickness of the films. Films of such thickness would be readily seen even at a magnification of no more than 500 diameters. The result, however, far from being useless, throws a flood of light on the question of the origin of the amorphous material.

Two explanations of the manner in which this is produced have been put forward. The idea of Rosenhain and Ewen involves the assumption of "crystal units" of definite size. Between adjacent crystals, spaces exist less than the crystal unit, in which therefore crystallization is impossible.

Humfrey's (17) explanation, which has always appeared more probable to the author, is as follows: ". . . When two crystals are gradually growing towards one another each will endeavour to marshal the . . . molecules surrounding it to its own orientation, and it would seem . . . that there would be formed between the two crystals a layer of matter in which the molecules are so arranged as to pass by gradual small displacements from the orientation of one crystal to that of the other." In such a case of gradual change from one "substance" to another the surface tension is greatly reduced. Thus T in equations (1) and (3) is not that calculated, but a distinctly smaller value. In each case d is proportional to T, with the result that the thicknesses of the amorphous film thus calculated should be

decidedly high. The results obtained thus lend strong support to this theory of the formation of the film.

So far as the actual values of the thickness are concerned, nothing more definite can be said than that they are probably nearly within the range of microscopic vision, i.e. of the order of 10^{-5} cm.

The author's sincerest thanks are due to Professor J. O. Arnold, D.Met., F.R.S., for his valuable interest and advice.

Bibliography.

(1) Beilby: *Phil. Mag.*, 1904, p. 258. The May Lecture, 1911, of the Inst. of Metals is a *résumé* of Dr. Beilby's work.

(2) Tammann: *Lehrbuch der Metallographie*, pp. 20–23 and 75–78.

(3) Rosenhain and Ewen: *J. Inst. Metals*, 1912 (2), vol. viii.

(4) Robertson and Cook: *Proc. Roy. Soc.*, 88, A, p. 462.

(5) Dalby: *Proc. Roy. Soc.*, 86, A, 1912, and 88, A, 1913.

(6) Hook: *Akad. Wiss. Wien Sitz*, 6, 108, 2, A, p. 1516, 1899.

(7) Smith: *J. Inst. Metals*, 1914 (2), vol. xii.

(8) Pascal and Journiaux: *Comptes Rendus*, 158, p. 414.

(9) Arnold: *Trans. Inst. Naval Architects*, 1908, p. 5.

(10) Traube: *Zeit. Anorg. Chem.*, 34, p. 413

(11) Hanriot: *Comptes Rendus*, 155, pp. 713 and 1502.

(12) Schottky: *Nachrichten der Kgl. Gesellschaft der Wiss. Göttingen, Math.-Physik. Klasse*, 1912.

(13) Rosenhain: *Engineering*, October 17, 1913, p. 539.

(14) Bengough and Hanson: *J. Inst. Met.*, 1914 (2), vol. xii.

(15) Huntington: *J. Inst. Met.*, 1912 (2), viii., p. 126.

(16) Benedicks: Doctorate Thesis, Upsala, 1904.

(17) Humfrey: *J. Iron and Steel Inst.*, Carnegie, vol. 5, p. 86.

The Metallurgical Department,
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DISCUSSION.

Dr. Cecil H. Desch (*communicated*): Mr. Thompson's paper affords an extremely interesting confirmation of the view, associated with the names of Quincke, Beilby, and Tammann, that surface tension exists in the boundary films between crystal grains. Too much importance must not be attached to the numerical values for the surface tension, in view of the great extrapolation necessary in making the calculations, especially in regard to the critical temperature. It would have been more satisfactory if the author had tabulated the data used in computing his figures. The present writer, in attempting to check the values for lead, obtained somewhat different results, using published data. It will be seen that small differences in the densities assumed for calculation lead to large differences in the critical temperatures.

However, a qualitative relation between elastic properties and surface tension seems to be established. Iron being a metal liable to show anomalies, it would be interesting to repeat the experiments on the influence of size of grain with some metal of simpler character, such as zinc or silver.

The introduction of a term representing the influence of surface films into the expression for the electrical conductivity is of distinct advantage, and lends itself well to experimental verification with other metals. Von

Weimarn goes so far as to explain the high resistance of solid solutions in the same manner, regarding them as colloidal systems of a high degree of dispersion. The author's view is, of course, quite independent of any such assumption.

It is to be hoped that the author will find an opportunity of extending his experiments, so as to increase the data for an examination of the question. Mr. S. W. Smith's determinations of the surface tensions of liquid metals are very valuable, and it is desirable that similar determinations should be made at several different temperatures for each metal, so that the surface tension at the ordinary temperature may be found by direct extrapolation, without having recourse to the critical temperature.

Mr. F. C. Thompson (*communicated reply*): Dr. Desch in his kind communication raises the question of how far the figures for the surface tensions of the amorphous films of the metals examined are reliable.

The difficulties involved in their calculation from the critical temperature of the metals were fully appreciated, and on p. 107 the author remarked: "The values of the critical temperatures arrived at in this way (i.e. from the densities) are certain to deviate markedly from the truth." An accurate knowledge of this constant, however, is not essential for the purpose. The surface tensions of the liquid metals have in general been determined experimentally at the freezing-point, a temperature so near the atmospheric, compared with the critical, that quite small increases only in the experimental values are necessary.

The subject is still engaging the author's attention, and a further communication may help to remove the existing difficulties.

SOME DIFFICULTIES IN VAN LAAR'S THEORY OF THE VAPOUR PRESSURES OF BINARY MIXTURES.

By R. T. LATTEY, B.Sc., M.A.

(*A Paper contributed to the* TRANSACTIONS *of the Faraday Society, May*, 1915.)

In recent years there has been considerable controversy between van Laar and Dolezalek regarding the interpretation of the isothermal vapour pressure curves of mixed liquids. The points of view of the disputants have been clearly summarized by F. H. Campbell.* Dolezalek and his pupils have used experimental data freely in support of their thesis, but van Laar has not tested his deductions from van der Waals' theorem in this way. To do so would involve a heavy expenditure of arithmetical labour; there are, however, certain simple deductions in the case of partially miscible liquids which enable us to test his theory with very little labour.

According to van Laar the partial pressure p_1 and p_2 of the vapours arising from a liquid containing $(1-x)$ and x molecular fractions of its components are given by the equations—

$$p_1 = P_1(1-x)e^{\frac{\beta x^2}{(1+rx)^2}}$$

or—

$$\log p_1 = \log P_1 + \log(1-x) + \frac{\beta x^2}{(1+rx)^2}$$

and—

$$p_2 = P_2 x e^{\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}}$$

or—

$$\log p_2 = \log P_2 + \log x + \frac{\beta(1-x)^2}{(1+r)(1+rx)^2}$$

where P_1 and P_2 are the vapour pressures of the pure components and β is a factor which diminishes with increase of temperature, while r is a constant depending on the nature of the fluids.

The total pressure P is therefore given by—

$$P = P_1(1-x)e^{\frac{\beta x^2}{(1+rx)^2}} + P_2 x e^{\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}}$$

On differentiating this we get—

$$\frac{dP}{dx} = P_1 e^{\frac{\beta x^2}{(1+rx)^2}}\left(1 - \frac{2\beta x(1-x)}{(1+rx)^3}\right) - P_2 e^{\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}}\left(1 - \frac{2\beta x(1-x)}{(1+rx)^3}\right).$$

The P/x graph will therefore pass through a maximum or a minimum when either—

$$P_1 e^{\frac{\beta x^2}{(1+rx)^2}} - P_2 e^{\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}} = 0$$

i.e.—

$$\log \frac{P_1}{P_2} = \frac{\beta(1-2x-rx^2)}{(1+r)(1+rx)^2} \quad \ldots\ldots\ldots \text{(i)}$$

or—

$$(1+rx)^3 = 2\beta x(1-x) \quad \ldots\ldots\ldots \text{(ii)}$$

* This journal, May 11, 1915.

Condition (i) applies to the common case where the curve exhibits a single maximum or minimum. Condition (ii) is also the condition that the partial pressure curves shall exhibit a maximum or minimum and is therefore impossible of practical realization. In cases where β and r have such values that equation (ii) has two roots x_1 and x_2 lying between 0 and 1, there will be separation into two layers, the composition of which may be represented by x' and x'', where $x' < x_1$ and $x'' > x_2$. Since these must give identical vapours, it follows that—

$$\log p_1 = \log P_1 + \log(1-x') + \frac{\beta x'^2}{(1+rx')^2} = \log P_1 + \log(1-x'') + \frac{\beta x''^2}{(1+rx'')^2}$$

$$\log p_2 = \log P_2 + \log x' + \frac{\beta(1-x')^2}{(1+r)(1+rx')^2} = \log P_2 + \log x'' + \frac{\beta(1-x'')^2}{(1+r)(1+rx'')^2}$$

and therefore—

$$\frac{\log(1-x') - \log(1-x'')}{\log x' - \log x''} = \frac{x' + x'' + 2rx'x''}{2rx'x'' + (1-r)(x'+x'') - 2} \quad . \quad . \quad \text{(iii)}$$

and—

$$\log(1-x') - \log(1-x'') = \frac{\beta(x''-x')(x'+x''+2rx'x'')}{(1+rx')^2(1+rx'')^2} \quad . \quad . \quad \text{(iv)}$$

A single determination of x' and x'' will therefore enable us to evaluate r and β at any given temperature.

There are many cases where two fluids are partially miscible above or below a certain critical temperature T_c and exhibit perfect miscibility at other temperatures. At the critical temperature x' and x'' must become identical in equation (iv), while equation (ii) must give a single solution for x_c, the critical composition.

Both these conditions are satisfied by the equations—

$$r = \frac{1-2x_c}{x_c(2-x_c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

and—

$$\beta_c = \frac{27(1-x_c)^2}{2x_c(2-x_c)^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

or—

$$\beta_c = \frac{27r^2(\sqrt{r^2+r+1}-1)^3}{2(r+1-\sqrt{r^2+r+1})(r-1+\sqrt{r^2+r+1})^3}.$$

Having obtained values of r and β_t at a temperature T° Abs. which is removed from the critical temperature, we can therefore calculate the value of β_c and hence of T_c, since $T/T_c = \beta_c/\beta_t$.

The solubility curve of methylethylketone and water is fairly accurately known from the determinations made by Rothmund * and by Marshall.† In the following table equations (v) and (vi) have been applied to calculate r, β, x_c, β_c and T_c. In the last column are given the values of βT which should be constant.

t° C.	x'.	x''.	r.	β.	x_c.	β_c.	T_c.	βT.
−30	0·17	0·65	0·35	3·305	0·41	2·98	269	803
0	0·10	0·695	0·45	4·055	0·36	3·51	315	1,110
30	0·06	0·69	0·81	5·785	0·30	4·555	385	1,750
60	0·052	0·63	1·14	7·135	0·25	5·565	427	2,380
90	0·052	0·53	1·47	8·135	0·22	6·775	436	2,950
120	0·059	0·41	1·61	8·035	0·205	7·21	438	3,160
150	0·125	0·19	2·16	9·14	0·17	4·09	428	3,860

* *Zeit. Phys. Chem.*, xxxvi, 1898, 433. † *J.C.S.*, 1900, 1350.

The values of x_c and T_c determined experimentally by Rothmund are $x_c = 0{\cdot}16$ and $T_c = 424°$ Abs. $= 151°$ C. Probably the most accurate solubility determination at any one temperature is that carried out by Marshall at 73·6° C. This gives the following results:—

$x' = 0{\cdot}05202$	$r = 1{\cdot}26$	$x_c = 0{\cdot}24$	$T_c = 426°$ Abs.
$x'' = 0{\cdot}5872$	$\beta = 7{\cdot}448$	$\beta_c = 6{\cdot}053$	

The calculation of T_c gives a fairly satisfactory result; but the value calculated for x_c cannot be reconciled with experimental data.

Taking the values $r = 1{\cdot}26$ and $\beta = 7{\cdot}448$, we can calculate the composition of the azeotrope which methylethylketone and water should give by using equation (i). This leads to $x = 0{\cdot}644$, whereas Marshall found $x = 0{\cdot}6606$.

If we use these constants to calculate the partial pressures of various mixtures, we obtain values which may be compared with Marshall's experimental data.

x.	Pressure of Ketone.		Pressure of Water.		Total Pressure.	
	Calculated.	Found.	Calculated.	Found.	Calculated.	Found.
0·0	0·0	0·0	—	273·0	—	273·0
0·052 }	437·0	495·8	263	263·6	701	759·4
0·587 }						
0·60	441	497·0	260	262·8	701	759·8
0·70	470	508	229	252·4	699	760·4
0·80	512	532·0	178·5	216·0	690·5	748·0
0·90	—	619·7	—	0·0	—	619·7

It is therefore clear that not only is the formula of van Laar inconsistent with the observed effects of temperature, but that it does not agree with experimental facts when the comparison is made at constant temperature.

REVIEWS OF BOOKS.

Practical Physical Chemistry. By ALEXANDER FINDLAY, D.Sc., Ph.D. Third Edition. (London, 1914 : Longmans, Green & Co. Pp. xvi + 327. Price 4s. 6d. net.)

Findlay's Practical Physical Chemistry was the first adequate textbook on the subject in English, and during the nine years which have elapsed since its first publication it has rendered indispensable service. Owing to the larger amount of time which is now devoted to the subject, the author has added several fresh subjects of study and new experimental methods such as the determination of vapour densities by the methods of Blackman and Menzies, the electrical heating and control of thermostats, the determination of the molar weight of dissolved substances by measurements of the vapour pressure and the measurement of decomposition and of ionic discharge potentials. The descriptions are clear and concise, and the value of the book is considerably increased by the insertion of a number of references to the literature. Although during the last few years several other books on the same subject have appeared, the new and enlarged "Findlay" may confidently be expected to hold its own.

Surface Tension and Surface Energy and their Influence on Chemical Phenomena. By R. S. WILLOWS, M.A., D.Sc., and E. HATSCHEK. (London, 1915 : J. & A. Churchill. Pp. 80. Price 2s. 6d. net.)

This little book is based on a course of lectures delivered at the Sir John Cass Technical Institute and is reprinted from *The Chemical World*, that excellent monthly which had unfortunately to suspend publication on account of the war. Being intended for the average student of chemistry, the mathematical treatment of the subject is simpler than that usually adopted, but it is no less logical or clear, and even the advanced student may read this book with interest and profit. The book is divided into five chapters. Chapter I defines and discusses surface tension, surface energy, and intrinsic pressure ; Chapters II and III deal with the relations between surface tension and other physical and chemical constants ; Chapter IV is devoted chiefly to adsorption, and Chapter V to the relation between surface tension and electrical phenomena. No chemist can afford to be without knowledge of these subjects, and as a simple introduction to their study one cannot do better than read and absorb this admirable little booklet.

Electricity in Gases. By JOHN S. TOWNSEND, Wykeham Professor of Physics in the University of Oxford. (Oxford, 1915 : at the Clarendon Press. Pp. 496. Price 14s. net.)

Thirty years ago a few paragraphs or pages were enough to devote in any text-book to what was then known about the conduction of electricity in gases. To-day, so great has been the recent advance, a whole textbook is

not sufficient. The present volume is, indeed, only one of a group of six volumes in which several physicists are co-operating to deal with this subject and the subject of radiation in general. It is limited almost entirely to a description of the conductivity obtained in gases at ordinary temperatures and at pressures ranging from atmospheric pressure to pressures of the order of one millimetre, in which the discharges may be explained by the theory of ionization by collision ; to this is added a brief description of the principal experiments on cathode rays and positive rays obtained in high vacua, as the results are of importance in connection with the general theory of electrical conductivity.

The subject of ionization by collision is, of course, Professor Townsend's own, and this is the first occasion on which a full presentation of the theory and facts has been made, though a smaller volume on the same subject was published a few years ago ; much the same may be said about the effects of diffusion. But it conveys almost an erroneous impression to pick out any particular portions for special mention, because Professor Townsend can speak authoritatively on any part of the subject. He is well known also for the many ingenious methods which he has devised for his investigations.

It is not feasible to deal with the volume in detail, but it will be useful, nevertheless, to give a very short account of the ground covered. A brief introduction is followed by Chapter II, dealing with methods of producing ions in gases (Chemical actions, radioactive emanations, Röntgen rays, Becquerel rays, Lenard rays, ultra-violet rays, flames, incandescent metals). Chapter III discusses the motion of ions in gases in electric and magnetic fields, including effects of diffusion. In Chapter IV the methods of measuring the velocity of ions in an electric field are discussed, while in Chapter V a fuller examination of the diffusion of ions is made ; and in Chapter VI the phenomena of recombination. Chapter VII is devoted to the formation of clouds and the determination of the atomic charge (experiments of C. T. R. Wilson, H. A. Wilson, Millikan, etc.). The phenomena of ionization by collision are dealt with in Chapters VIII and IX. Chapter X embraces discharges between conductors of different shapes, and XI the different appearances presented in discharge tubes. The final chapter gives the brief description of cathode and positive rays and their properties alluded to before.

The whole subject is dealt with in an exhaustive fashion up to the most recent investigations, and the volume must needs be in the hands of every worker in this department of physics ; for while the greater part of it can be found in separate papers as published, no attempt has previously been made to give such an orderly account as we find here.

The book is excellently printed ; the diagrams are well drawn and remarkably clear. There appear to be only few misprints ; e.g. Döppler for Doppler, and Wichert (in Preface) for Wiechert. It is in every way a fine achievement.

Technical Methods of Chemical Analysis. By GEORGE LUNGE and C. H. KEANE. Vol. III. Parts 1 and 2. (London, 1914 : Gurney & Jackson. Pp. 1,125. Price £3 3s. net.)

Volume III of this monumental treatise, which requires to be divided into two parts owing to the large number of pages it covers, is the concluding volume of the English edition of this work.

The subjects included are taken from the third and fourth German edition, published in 1910–11, and have been brought up to date by the translator, who is thus collaborator. Some sections, in fact, have been entirely

re-written for the English edition. This is, in some cases, essential, because the processes of manufacture and the analytical methods employed in this country are quite different from those pertaining to Germany.

In a work of this kind, embracing the whole of the methods of technical analysis as applied to manufactures, it is obviously not possible to review at length, but from having used the earlier volumes in our laboratory ever since they were published, we can vouch for the great value of the books and of the methods therein set out.

An examination of the present volume enhances our respect for Professor Lunge, and we are only voicing the obvious when we say that all technical chemists owe a debt of gratitude to Professor Lunge and to his English collaborator—Dr. Keane.

The volume deals with, amongst other subjects, Mineral Oils, Lubricants; Oil Fats and Waxes; Special Methods of Analysis employed in the Oil and Fat Industries; Drugs and Galenical Preparations; Essential Oils; Organic Preparations; India-rubber and Rubber Goods; Leather; Sugar; Alcohol; Wine; Paper and Inorganic Colours.

We have only one complaint to make. In order to find the index it is necessary to consult Part II of the volume. As the books are large and heavy this is an inconvenience. The extra index would well repay the extra trouble involved. This little grumble on one side, we hail the new work with the greatest pleasure and congratulate the authors and publishers upon its completion.

Technical Gas Analysis. By GEORGE LUNGE, Ph.D. (London, 1914: Gurney and Jackson. Pp. 407. Price 15s. net.)

This new work by Dr. Lunge undoubtedly meets a want, since, unlike some other works on gas analysis which are devoted mainly to the work of the author, Dr. Lunge has written a book which, although not embracing all that has been published on the subject, presents it in a broad manner.

Many different types of apparatus are described, and the particular class of work for which they are best adapted is pointed out. In gas analysis much depends upon certain factors, speed of work and accuracy being the most important, and it is very often not easy to combine the two. For example, Hemples and Orsats' apparatus are both rapid and easy of manipulation, but they lack the accuracy of that of Bone and Wheeler.

Dr. Lunge has himself carried out much valuable work in connection with gas analysis, consequently his opinions carry great weight, and for this reason alone the book has a special value.

A careful study of the work shows us that all the most useful and approved methods are included, and we do not notice that anything of importance has been omitted.

The methods are very clearly described, and no technical library claiming to be up to date will be complete without this very valuable treatise. This book adds another to the library of technical books which the chemical world owes to Dr. George Lunge.

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THE TRANSFORMATIONS OF PURE IRON.

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Tuesday, October 19, 1915, at the Institution of Electrical Engineers, Victoria Embankment, London, W.C., a **General Discussion** took place on **The Transformations of Pure Iron. Sir Robert Hadfield, F.R.S., President**, was in the Chair.

OPENING ADDRESS.

BY SIR ROBERT HADFIELD.

The proceedings were opened by the **Chairman**, who delivered the following address :—

With reference to the very interesting paper now presented by Dr. A. E. Oxley, of the Sheffield University, to whom we are much indebted for the trouble he has taken, it seems to me that he is putting forward theories which well deserve our careful consideration.

Professor Weiss, of Zurich, has written several valuable papers on the subject of magnetons. Not only is his theory ingenious, but it seems to be suggestive of what is really happening, that is, admitting that the electron and magneton theories themselves, quite apart from their bearing on our particular subject, are eventually found to be correct.

Dr. Oxley appears to have taken up this particular line of thought, and seems to me to have brought this home to our minds in a very clear and practical manner, that is when it is remembered

that it is at present purely theoretical ; theory, however, often goes before practice.

Without wishing to introduce controversial points, it is, however, necessary to say that Dr. Oxley—at any rate it seems so to me, and others share this feeling—has presented a case which shows that the other critical point of iron, the so-called A_3 point, can also be explained without calling in the aid of allotropy, thus throwing considerable doubt on allotropy as an explanation for the phenomena met with in the many curious properties of iron alloys, which allotropic explanations have been based almost entirely on the allotropic explanations of the critical points in iron itself.

The allotropic theory has hopelessly broken down, and beta iron has disappeared. As is well known, to explain the curious phenomenon of hardening this form of iron called "beta" was invoked. It was, however, found that this did not suffice, and another form was raised called "gamma." Even these were insufficient, and it was suggested that there was a fourth form, "delta." In other words, so it seems to me, the theory, interesting and valuable as it has been in invoking discussion and giving rise to research, has broken down. It is admitted that the carbonist point of view has not explained all the difficulties met with, but nevertheless it has gone upon more tangible lines. We know of the existence of carbides, also their properties and characteristics are well known, and they can be isolated. No one has ever seen or handled the so-called allotropic forms of iron. In this direction there could not have been more valuable aid to research than the following papers by Dr. J. O. Arnold, F.R.S., and Dr. A. A. Read. The research work was carried out in the Metallurgical Departments of the Sheffield University and the University College, Cardiff.

It was owing to the importance of this subject, that is the nature and type of different carbides, the writer of these notes offered in this country and on the Continent, also in America, and also to the Metallurgical Division of the Applied Science Department of the Sheffield University, where Dr. Arnold carried on his work, three separate research prizes in the hope that these would stimulate further research in this desirable direction, for surely after the classic work of Abel, Hughes, Arnold, Read, Hogg, Stead, Edwards, Parry, McCance, Carpenter, further aided by Metcalf, Howe, Jullien, T. Sterry Hunt, and Campbell in America, Ledebur, Müller, Osmond, le Chatelier, Pourcel, Ackerman, and others on the Continent, the rising generation will not rest satisfied until they have torn the veil from one of Nature's most profound and interesting secrets as to why steel containing sufficient carbon turns from a comparatively soft material to one possessing glass-

scratching hardness after being heated to certain well-known temperatures and quenched or cooled quickly. The reverse phenomenon is also just as interesting, that is to say, upon taking such a specimen it can be just as quickly restored to its former soft condition by heating and cooling down.

PRÉCIS OF VARIOUS PAPERS BY DR. J. O. ARNOLD, F.R.S., AND DR. A. A. READ.

RESEARCHES ON THE CARBIDES OF STEEL.

	Title.	Read before.	Date.
1.	The Chemical Relations of Carbon and Iron	Chemical Society	1894
2.	The Chemical and Mechanical Relations of Iron, Manganese, and Carbon	Iron and Steel Institute	1910
3.	The Chemical and Mechanical Relations of Iron, Chromium, and Carbon	Iron and Steel Institute	1911
4.	The Chemical and Mechanical Relations of Iron, Vanadium, and Carbon	Iron and Steel Institute	1912
5.	The Chemical and Mechanical Relations of Iron, Tungsten, and Carbon, and of Iron, Nickel, and Carbon	Institution of Mechanical Engineers	1914
6.	The Chemical and Mechanical Relations of Iron, Cobalt, and Carbon	Institution of Mechanical Engineers	1915

In the same manner, equally interesting and probably concerned with the same problem are the extraordinary results obtained with certain alloys of iron. For example, manganese steel, which is non-magnetic, can be made magnetic by certain heat treatment described in several of my papers, while certain alloys of iron with nickel, also iron with nickel and manganese, possess electrical and magnetic qualities of a peculiar nature.

If Dr. Oxley can throw light on these problems by his very excellent and carefully thought-out theory, coming as it does in what may be termed quite a new direction, he will have rendered great service, for underlying theoretical consideration are the important facts of practical application. Whilst it is true the correct understanding of the heat treatment of steel controlling and varying the temperatures to which it is heated to obtain certain desired physical properties has advanced with marvellous rapidity during the last ten years, thanks very largely to such men as Osmond, H. le Chatelier, Arnold, Roberts-Austen, Callendar,

Howe, Stead, Burgess, and others, there is still much to be learned, still much unexplained, in the many curious problems met with.

I will not here discuss Dr. Oxley's theories, that is for those present at the meeting; but I would like to say that it would appear to be in some new direction, such as that set forth by Dr. Oxley, where we shall have to look for advancing our knowledge. Thus this discussion may be the starting-point of quite a new line of thought, which, whilst it will leave the allotropist and the carbonist each to go on his own way and continue his useful researches, may eventually bring them together and help to find a common and correct explanation.

ON THE TRANSFORMATIONS OF PURE IRON—INTRODUCTORY PAPER.

Mr. A. E. Oxley, M.A., D.Sc., Lecturer in Physics in the University of Sheffield, then read the following Paper as an Introduction to the General Discussion.

The present communication is composed for the most part of extracts from letters to Sir Robert Hadfield, and deals with the nature of the molecular constitution of pure iron. At Sir Robert's suggestion these extracts are presented to the Faraday Society.

It is now believed by a large school of metallurgists that the A_2 transformation can be satisfactorily explained without assuming allotropic change. The A_3 transformation, on the other hand, is generally regarded as involving allotropy.

The crystalline state is one of extreme molecular association (physical polymerism or the grouping of chemical molecules under the influence of mutual physical forces), and if allotropy is determined solely by the nature and extent of this association, each substance will show an unlimited number of allotropic forms within a finite temperature interval. In some experiments on "The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility," * I have frequently been led to the conclusion that the molecules of crystalline, and even of liquid, substances are in a distorted state. This distortion is always very slight, and is due to the action of restraining forces exerted by neighbouring molecules on each molecule of the material medium. It is clear, therefore, that the configuration of a molecule in a crystalline medium is slightly different from that of a molecule of the same substance in the liquid. If the mutual influences of the molecules were withdrawn, the molecules of both states would alter their configurations slightly and would become identical. Such a relationship between the molecules is of the nature I have previously called "crystalline grouping," and the distorted condition of the molecule is not to be regarded as indicating allotropy. If, indeed, allotropy were determined in this way, then every degree of association would imply a new allotropic form, the number of which forms would be infinite for each substance throughout a finite interval of temperature and "allotropy" would be a useless term.

To surmount the difficulty presented by the existence of so many allotropes, two different types of allotropy have been recognized: (1) The two-phase (discontinuous) type, (2) the one-phase (continuous) type.†

Benedicks says: "At present the binary state diagrams (temperature-concentration) rest entirely on the phase doctrine as a basis. As is well known, they have for this reason regard only to the equilibrium between phases (heterogeneous equilibrium), no consideration is taken of the internal molecular (homogeneous) equilibrium within each phase, as that is, on the whole, not dealt with in the phase doctrine as developed by Gibbs. We must then take as a fact, at least for the present, and generally speaking, that

* A. E. Oxley, *Phil. Trans. Roy. Soc.*, A, vol. 214, p. 109, 1914, and ibid., A, vol. 215, p. 79, 1915.

† *Vide* Benedicks, *Journ. Iron and Steel Inst.*, vol. lxxxix., p. 407, 1914.

internal molecular transformations cannot be illustrated in our (two-dimensional) state diagrams for two components."

I do not wish to give reasons against the adoption of such conceptions, but having once recognized them it is of the utmost importance to distinguish experimentally between them. This leads us to the large mass of admirable experimental work which has been carried out during recent years, to problems which have been courageously attacked, but involving, it seems, insuperable difficulties.

To show experimentally that a discontinuity in any one property exists is an exceedingly difficult problem, and it does not seem that any method within our power will satisfy an opponent. A reference to the recent work of Honda* on the variation of magnetization with temperature in the neighbourhood of A_3 will illustrate this point.

Leaving aside the transformations of iron for a moment, the fusion-point of a substance is perhaps the nearest approach to a mathematical discontinuity defining the two-phase type of allotropy. But to those who have had the opportunity of examining Lehmann's liquid crystalline state, under the crystallization microscope, it hardly seems that even in this extreme case the fusion-point of ordinary substances can really involve a discontinuity of the kind required by the definition. The liquid crystalline state discloses, as it were, a magnified image of the process which must be going on in all liquids before crystallization, viz. a continuous marshalling of the molecules (perhaps in some cases a labile state is formed which may or may not be doubly refracting) into a flowing space lattice which eventually becomes a rigid crystal. One of these liquid crystal compounds I examined showed no liquid crystalline state on fusion, but did so on re-cooling over a considerable range prior to crystallization in the ordinary sense. Such a substance exhibits two-phase allotropy on heating, one-phase allotropy on cooling, if we examine the rate of growth of the crystalline structure. It is interesting to note that the crystals produced by the one-phase allotropic transformation pass again into the liquid by the two-phase allotropic transformation and that the process can be repeated.

In other words, a property may change rapidly (i.e. in a small temperature interval), but we have no evidence to show that it is discontinuous.

It seems therefore that a sharp distinction cannot be made between these two types of allotropy. The changes observed appear to be better and less vaguely expressed as different degrees of molecular association—the idea of molecular association being continuous.

I have come to the conclusion, from a consideration of the facts, that the mutual influences of the molecules, i.e. the molecular association (physical polymerism) is alone sufficient to account for the phenomena observed. There still remains the possibility that these phenomena may be connected with some intra-molecular change. Such an alteration of the atomic structure of the molecule would be allotropic in the sense of the oxygen to ozone transformation or in the sense of the transformation from one isomer to another. This criterion of allotropy has been adopted and, from the magnetic and thermal points of view, an attempt is made in what follows to show that allotropy in this sense is absent in the transformations which are of interest to the iron and steel metallurgist.

If the molecule of the crystalline structure, on *withdrawal of the restraining forces*, differs in configuration from a free molecule which has originated in some other way (say by an independent chemical or physical

* *Journ. Iron and Steel Inst.*, 1915, and *Science Reports*, Tokio, vol. iv., No. 3, p. 261, 1915.

process), either as regards the integral number of atoms in the molecule or the relative distribution of those atoms, even if their number remains the same, then the substance exhibits allotropy. As examples we may take the oxygen to ozone transformation and the many types of isomers known to organic chemistry. Not only has an allotropic modification characteristic physical properties, but, to some extent, characteristic chemical properties too. The constitutional formulæ of modern chemistry are founded on the assumption that the properties of a substance are determined by the nature, number, and mutual dispositions of the atoms within the molecule.

Now the crystalline forms of allotropic modifications will be characteristic, for the space lattice will be conditioned by the configuration of the molecule which determines the restraining forces.* On the other hand it has been shown † that *molecules of exactly the same configuration* may be packed into quite distinct crystalline aggregates, of different degrees of stability, so that a difference of crystalline symmetry does not necessarily imply allotropy in the sense defined above.

It should be pointed out that this definition is not specially designed to meet magnetic considerations ; it is consistent with the recognized chemical view. We must distinguish between the forces holding the molecules in position in the crystalline structure and those holding the atoms together in the molecule,‡ and if the latter forces are large compared with the former (thermo-chemical evidence that this is so will be given later), then the preservation of molecular identity, and hence the rarity of allotropic change, will not be a surprising phenomenon.

The above remarks lead us to a criterion by which the nature of the so-called β to γ transformation may be discussed. Weiss § has shown that the magnetic properties of β and γ iron can be interpreted in terms of a simple atomic constitution of the iron molecule, and the point of importance for us is that the iron molecule consists of two atoms in the temperature intervals of stability of the β and γ forms, and therefore through the transformation from paramagnetic γ iron to ferro-magnetic β iron there is no change in the integral number of atoms constituting the iron molecule. Weiss's work shows that each state of iron provides a measure of the constant of Curie (C), the parameter of the hyperbolæ representing the variation of specific susceptibility as a function of the absolute temperature. In conclusion he states :—

"Le passage du fer β au fer γ qui correspond à la perte des actions magnétiques mutuelles sans variation du nombre des atomes de la molécule reste à expliquer, mais la concordance des diverses valeurs de C ne peut être due au hasard."

Hence in so far as the integral number of atoms in the molecule is concerned we cannot regard A_3 as an allotropic change-point.

It is interesting to note that Barlow and Pope ‖ have pointed out that those elements which crystallize in forms of high symmetry are the ones which show the least tendency to form allotropic modifications. Iron is known to crystallize throughout the β and γ ranges in the cubic system Further, Retgers ¶ has shown that the higher the crystalline symmetry of a particular element the smaller, as a rule, is the number of atoms contained in

* *Phil. Trans. Roy. Soc.*, A, vol. 215, p. 79, 1915.
† Barlow and Pope, *Trans. Chem. Soc.*, vol. lxxxix., p. 1741, 1906.
‡ Ibid., *loc. cit.*
§ *Comptes Rendus*, vol. cxliv., p. 25, January 1907.
‖ *Loc. cit.*, p. 1741.
¶ *Zeitschr. Phys. Chem.*, vol. xiv., p. 1, 1894. The rule holds for 85 per cent. of the elements.

the molecule. These points are consistent, and are in favour of absence of allotropy in iron.

The simple atomic constitution of the iron molecule makes it improbable that changes of physical properties of iron can be due to a rearrangement of the atoms in the molecule. It is conceivable that the two atoms may be slightly displaced relative to one another as the transformation points are passed, but we cannot regard the resulting iron molecule as a distinct type possessing a new set of properties. Moreover, from a magnetic point of view, assuming that magnetism is to be ascribed to polar molecules, however this polarity may originate, the appearance of ferro-magnetism on cooling could not be explained on such a view. Ferro-magnetism demands inter-molecular forces—the forces of crystallization—although no one doubts that inter-molecular forces and intra-molecular forces are inseparable,* and that a small change in the latter may accompany and indeed is essential in a re-grouping of the molecules. If we imagine the inter-molecular restraining forces abstracted, then the molecules of the β and γ forms of iron would be absolutely identical.

If there is no abrupt change of the atomic constitution of the iron molecule, then changes of the properties of pure iron such as occur at A_3 must be ascribed to a change of crystalline grouping of the molecules. This change must be of such a nature that the crystalline symmetry is not affected on passing A_3; a change of the closeness of packing of the molecules is all that is required. If the cooling through A_3 is accompanied by a closer grouping of the molecules in the direction (which is characteristic for each crystal) of spontaneous magnetization, there will be no change of crystalline symmetry, while the increased interaction between the molecules will give rise to spontaneous magnetization. The variation of molecular distances in the directions perpendicular to that of spontaneous magnetization for an individual crystal is of small importance from a magnetic point of view, for each molecule is mainly constrained by the molecule in front and the one behind in the direction of its magnetic axis.† Thus this interpretation is not necessarily inconsistent with known magneto-striction data or with determinations of thermal expansion (linear or volume) of a *mass* of iron crystals.

If there is a change of molecular arrangement at A_3, then on passing this point there will be a thermal effect determined by the difference between the internal potential energies above and below A_3. There may be an accompanying molecular distortion, but this will be slight, and (as pointed out on p. 4) cannot be regarded as implying allotropy.

The thermal energy evolved on cooling through A_3 is just the heat of transformation from a more open to a closer packed cubic system, as described above, with probably a small contribution from intra-molecular adjustment *resulting from the change of packing*. As already pointed out, these two parts of the thermal evolution are inseparable, but the existence of the second part does not justify the existence of a new type of iron molecule. Accompanying the re-grouping, the iron molecule takes up a slightly distorted appearance of the iron molecule on the other side of A_3. Under pressure we should no doubt get a slightly different re-grouping of the molecules, and, as a consequence, a slight variation of the atomic separation in the molecule. This variation of separation will be different for different pressures, and, therefore, like the phenomenon of association mentioned on p. 129, cannot be regarded as implying allotropic change.

It is known that the transformations from ozone to oxygen and from white

* *Phil. Trans. Roy. Soc.*, A, vol. 215, p. 100, 1915.

† Ewing, *Magnetic Induction in Iron and Other Metals*, 3rd edition, p. 310.

phosphorus to red are exothermic. The thermal evolutions accompanying allotropic and isomeric changes are comparable with the heats of formation of chemical compounds, and are *in general* large compared with those involved in the passage from the liquid to the crystalline state or from one crystalline state to another.* The following are some values of the thermal evolution accompanying known allotropic and isomeric changes :—

Allotropic { 96 grams ozone = 96 grams oxygen + 59,200 gr.cals.
31 grams yellow phosphorus = 31 grams red phosphorus + 21,000 gr.cals.

Isomeric { 78 grams dipropargyl = 78 grams benzene + 100,000 gr.cals.
58 grams allyl alcohol = 58 grams acetone + 18,600 gr.cals.
= 58 grams propaldehyde + 22,600 gr.cals.

With these may be compared the following values of the latent heats of fusion of some elements † :—

Element.	Latent Heat (gr.cals.).
Bismuth	13
Cadmium...	14
Lead	5
Silver	22
Tin	14
Zinc	28
Gallium	19
Phosphorus	5

These latter values are comparable with the thermal evolution during the transformations of pure iron. From the recalescence curves given by Dr. Arnold ‡ for this substance the rise of temperature is largest for the A_3 transformation point, and is approximately 14° C. Hence, taking the specific heat of iron as 0·1, the thermal evolution at A_3 is 1·4 gr.cals. This small thermal evolution favours the view expressed above that the A_3 transition involves a molecular re-grouping, similar to that which occurs in the ordinary process of crystallization, rather than a re-building of the internal structure of the molecule. Therefore from the thermal point of view also, allotropic change, as defined in the present Paper, appears to be absent at A_3.

The coexistence of thermal expansion and thermal evolution on cooling through A_3 cannot be advanced as an objection to the views developed above, for the same phenomena accompany one another during the transition from water to ice.

The criterion we have adopted does not thrust upon us the difficulty of determining what is happening *at* a given temperature but upon the *sum total of what has happened during an interval of temperature*, which may be large or small, between the two states examined.

In the physical aggregation of molecules we are concerned with residual forces between two or more identical systems. The result is a slight distortion of each system, such as occurs to a small extent in the liquid state and to a larger extent in the crystalline state. In chemical combination we are concerned with a stronger and more direct action between two different systems, resulting probably in a local charging up of each system.

Let us now push our definition of allotropy one step further, and refer it not to the atomic structure of the molecule but to the electric and magnetic structure of the atom. From this point of view the iron atom in iron-

* Pattison Muir, *Elements of Thermal Chemistry*, pp. 250–3.
† *Recueil des Constantes Physiques*, Paris, 1913, pp. 323–4.
‡ *On a Fourth Recalescence in Steel*, B.A. Report, Sheffield, 1910.

carbonyl ($Fe(CO)_5$) is quite different from the iron atom in ferrous chloride ($Fe(Cl)_2$). The latter compound is strongly paramagnetic, the former is diamagnetic; although chlorine and the group CO are each diamagnetic. Do we not here have a kind of atomic allotropy? In this sense the allotropic theory may be consistent with the carbide theory which attributes the properties of carbon steels to definite compounds of iron with carbon (such as cementite, Fe_3C).

I am much indebted to Sir Robert Hadfield, first for suggesting the application of the results of my earlier work to the transformation-points of iron, and second for the encouragement he has given me throughout the whole of our correspondence.

The Allotropy of Iron.

Mr. F. C. Thompson, M.Met., B.Sc. (University of Sheffield), sent the following communication on "The Allotropy of Iron" as a contribution to the Discussion.

Since the appearance of the exceedingly important work by Burgess and Crowe* on the heating and cooling curves of very pure iron, the thermal changes accompanying the allotropic ones in that metal may be regarded as finally settled. The curves published are, with the exception of the single peak at Ar_2, in complete agreement with the results of Arnold, but in view of the importance of the definite establishment of the existence of the thermal point Ac_2, an independent curve is here reproduced (Fig. 1). The specimen on which the curve was taken was an exceedingly pure sample of American ingot iron made several years ago. The analysis, according to Mr. W. Bagnall, B.Met., who very kindly placed the material at the author's disposal, is :—

Carbon per Cent.	Silicon per Cent.	Manganese per Cent.	Sulphur per Cent.	Phosphorus per Cent.	Copper per Cent.	Fe per Cent. by Difference.
less than 0·01	trace	trace	trace	trace	0·02	99·97

A micrographic examination revealed merely the allotriomorphic crystals of iron without even traces of carbide, sulphide, or slag. The heating curve here reproduced was the third successive one taken *in vacuo*. The evolution of gas during heating had almost ceased, and the third and fourth curves were identical. The experiment was conducted with the new potentiometric apparatus recently installed by Professor J. O. Arnold, D.Met., F.R.S., and readings were taken telescopically about every 2° C. The existence of the point Ac_3 is obvious at 765° C., Ac_3 being at 920° C.

The definite proof of the existence of the thermal point Ac_2 robs of much of its weight the argument of Benedicks† against the allotropy of β iron. The evolution of heat at this point‡ in what is almost chemically pure iron can be due to nothing but an atomic or molecular rearrangement. As a result of their work the investigators first mentioned§ say : ". . . Nevertheless all the

* Burgess and Crowe, *Proc. Am. Phys. Soc.*, II, 5, p. 404, November, 1913.

† Benedicks, *Journ. Iron and Steel Inst.*, II, 1912, p. 242.

‡ The weight of the piece used was about 20 grams, which robs the curve of the beautiful sharpness of those taken by Burgess and Crowe using 0·7 grams only.

§ Burgess and Crowe, loc. cit.

physical properties of iron which have been studied, with the single notable exception of crystallographic structure, have shown, in the hands of one or more skilful experimenters, a distinct discontinuity for the lower critical range A_2 as well as for the upper A_3 range. For several of the phenomena, such as electrical resistance, thermo-electricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for A_2 as for A_3, while the thermal effect has, of course, been long recognized as being much the more pronounced at A_3."

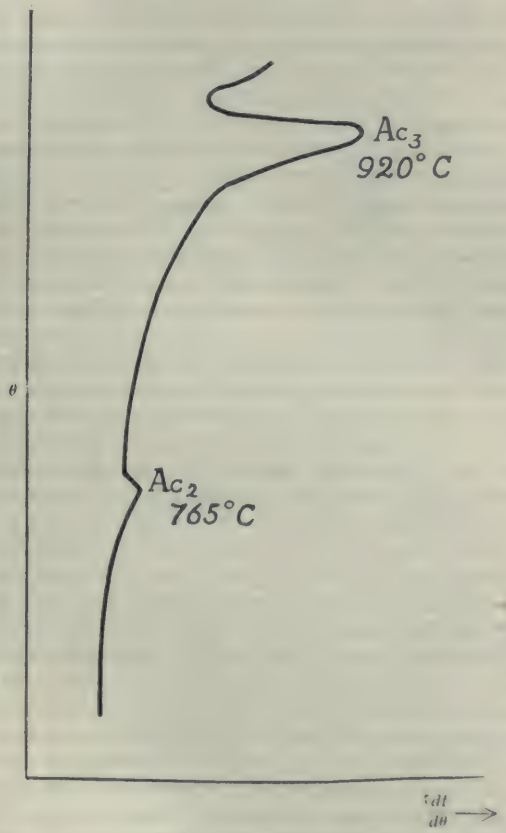


FIG. 1.—Heating Curve.

Ingot Iron, 99·97 per cent. Fe.

It was also found impossible to eliminate or attenuate A_2 by thermal treatment, a result incompatible with any theory of β iron as undercooled γ iron, and, in addition, occluded gases, to which at various times so many effects have been attributed, exert no essential action on either point.

The points A_2 and A_3, although by far the most important, are by no means the only ones at which discontinuity in a physical property or properties has been observed. With regard to the thermal point which has been supposed to exist in the neighbourhood of 600° C., the author has been unable to observe it in spite of repeated endeavours with pyrometric appliances of the highest degree of sensitiveness, a result in accord

with those of several other workers. At or about 830° C., however, a marked discontinuity in the magnetic properties of iron has been detected by both Curie and Weiss and Foex.* Benedicks† also at the same temperature has observed a bending off in the dilatation curves of iron, so that still further complication of the properties of iron at high temperatures is possible. At temperatures approaching a white heat, another, and more definite, point, first suspected many years ago, seems now to be definitely established as a result of the work of Ruer and Klesper,‡ and δ iron must take its place along with α, β, and γ. This point, first detected by Ball§ in the neighbourhood of 1,300° C., was ascribed by Osmond‖ to oxidation of the samples, but Curie's discovery of a change of magnetic properties of pure iron in the same temperature region indicated that the "Ball" point was a true allotropic change. The pyrometric uncertainties of the earlier workers caused the point to be ascribed to a temperature about 100° C. too low, and the most exact work of Ruer and Klesper, confirmed by several other individual observers, shows that in pure iron the change from γ to δ occurs at 1,400° C. This change, like that from α to β, is essentially reversible on heating and cooling. The influence of carbon in raising the temperature at which this transformation occurs is unexpected, and in mild steels certain difficulties of interpretation are still existent, but the occurrence of the fourth δ modification of pure iron seems now to be definitely proved.

The experimental material discussed above will now probably be accepted by most metallographers, but the interpretation of the facts from the point of view of the theory of allotropy is a different matter.

The extremely interesting and valuable paper of Dr. Oxley reopens the discussion of the validity of the assumption that the thermal and other changes are evidences of the existence of the allotropic modifications of iron. β iron has already borne the weight of many attacks, but the new battle-line extends to γ iron as well. To a certain extent the question of whether iron at 800° C. and iron at 1,000° C. are allotropes must remain one of definition, but in the present case there is more than this, and, whether the α, β, γ, and δ forms of iron are allotropic or not, Dr. Oxley has shown beyond doubt that the nature of the allotropy is essentially distinct from that involved in the transformation from oxygen to ozone. The new definition of allotropy is on a very different plane from, for instance, Nernst's definition as a *sudden* change in internal energy, and is apparently much more narrow, so much so as to cut out almost every example of allotropy in metals, and also such a typically allotropic change as the transition from rhombic to monoclinic sulphur. It eliminates as allotropic the changes in tin which have up to the present been regarded as classical examples of such transformations in metals. A total recrystallization with a different system, e.g. rhombic to tetragonal, involving a *sudden* change of volume amounting to 30 per cent., together with alterations of electromotive force, electrical resistance, specific heat, and thermo-electric power, do not, according to Dr. Oxley, denote allotropy, since the heat change accompanying them is small. Such a standpoint will result merely in a multiplication of terms, since some other name must be found for changes of this kind.

Adopting, however, for the time being, the definition which Dr. Oxley

* Weiss and Foex, *Arch. Sci. Phys. Nat.*, **4**, 1911, 31, pp. 4, 89.
† Benedicks, *Journ. Iron and Steel Inst.*, I, 1914, p. 430.
‡ Ruer and Klesper, *Ferrum*, June, 1914, **9**, p. 257.
§ Ball, *Journ. Iron and Steel Inst.*, I, 1890, p. 85.
‖ Osmond, ibid., p. 102.

proposes, the only definite evidence of which the author is aware regarding the intra-molecular structure of the different forms of iron is the work of Weiss summarized in the *Transactions* of this Society for 1912.* As a result of his work on the "magneton" Weiss arrived at the following conclusion :—

"The experiments made on β iron have shown that its molecule is Fe_3, that of γ iron Fe_2, and that of δ iron is probably Fe. In nickel and cobalt the molecule above the Curie point is composed of a single atom. The magnetic forms have probably three atoms per molecule."

This is the view of Weiss in 1912, arrived at from the magneton theory five years later than that which is quoted by Dr. Oxley, that the transformation from paramagnetic γ iron to ferromagnetic δ iron is unaccompanied by any atomic change.

The researches of Honda† have failed to confirm the existence of the magneton, but for the present, and until further results are available, the work of Weiss regarding the constitution of the various modifications of iron is the only direct evidence available. Additional interest attaches to these results in that the evidence in favour of a fourth variety of iron, stable only at exceedingly high temperatures, is strongly confirmed. In a private discussion with Dr. Oxley the latter has suggested a way, however, in which the two antagonistic views of Weiss may be reconciled.

The American investigators whose work has already been quoted have endeavoured to exclude β iron from the position of a definite allotrope, since crystallographically it is regarded as strictly isomorphous with α iron.‡ This was the conclusion arrived at by Osmond and Cartaud § as a result of their experiments on the reduction of iron salts at temperatures within the different critical ranges. The same investigators, however, were able later ‖ to amplify these results, and were able to interpret their newer work on the figures produced in iron by plastic deformation, on twinning, etc., as follows :—

"One is led to think that the mesh of α iron is a simple cube, and that of γ iron a cube with centred faces ; then that of β iron would be a centred cube. The only positive conclusion that we can draw from these researches is that *the three (α, β, and γ) allotropic varieties of iron, although they all crystallize in the cubic system, present well-marked specific characters, and cannot have the same internal structure.*"

These crystallographic results point merely to a different mode of packing of the iron molecules, which, beyond suffering slight distortion as a result, might be essentially unaltered. The magnetic work of Weiss has rendered it highly probable, however, that the differences extend beyond the mere molecular packing, each molecule having a definitely different atomicity. Combining these two results, the question of the allotropy of iron seems to have been placed beyond question.

If the paper of Dr. Oxley had been confined to no more than the novel and extremely valuable thermal argument concerning allotropy, it would have been of the highest service in arriving at definite conclusions. His new line of thought is of immense help in affording an insight into the whole question. The results, taken as a whole, are decidedly antagonistic to the allotropic standpoint, and at any rate the immense advance has been made that the allotropy of iron and that of oxygen differ in essentials.

It may be doubted, however, whether the evidence is so overwhelmingly

* Vol. viii., p. 153.
† Honda and Takagi, *Jour. Iron and Steel Inst.*, I, 1915.
‡ Burgess and Crowe, loc. cit.
§ Osmond and Cartaud, *The Crystallization of Iron.*
‖ Ibid., *Jour. Iron and Steel Inst.*, III, 1906, p. 486.

against the allotropy of iron as Dr. Oxley himself thinks. In the first place, a definition of allotropy which will, in practice, depend on whether the accompanying heat change is large or small is somewhat unsatisfactory. To the author, a definition such as the one due to Nernst, based on *sudden* changes of physical or chemical properties, appears far more workable. If Nernst's view be adopted that an allotropic change is one resulting in a *sudden* change of internal energy, the allotropy of iron is established. Again, the application of Dr. Oxley's thermal test to the allotropic changes in iron, and equally in other metals, is complicated by the fact that the heat effect observed is the algebraical sum of several changes of which the allotropic change is only one. At Ar_3, when γ iron changes to β, a "decrystallization" of the γ iron and a recrystallization of the amorphous material which results to form β iron crystals also occur, both changes from which thermal evolutions or absorptions may be expected. To state exactly the quantity of heat evolved, due solely to the change of allotropic form, is therefore a matter of difficulty. The most serious objection to the thermal solution appears to be the fact that practically every case of well-defined metallic allotropy is excluded, the fate also of other examples in non-metallic elements which have been regarded as typical. Among the metals no example of allotropy has been examined more carefully, nor apparently received stronger confirmation, than the change from grey to white tin. The remarkably important physical changes which result from this transformation are too well known to need repetition,* but the heat change per gram at 0° C. is only 4·5 gm.-cals.† The thermal argument of Dr. Oxley would make this change, therefore, inter-molecular rather than intra-molecular, and hence not allotropic, Similarly, the heat change per gram in the change from α cadmium to γ‡ cadmium is only 6·6 gm.-cals., whence the allotropic nature of this change would also be denied. *The final proof that this definition of allotropy is too narrow is obtained from the fact that, since the heat change per gram is but 3·2 gm.-cals.,§ the transition from rhombic to monoclinic sulphur is not an allotropic one.*

Two further points may deserve brief reference. The relationship which the temperature at which allotropic changes take place bears to the pressure and to the presence of dissolved substances is well known, and it is of interest to discover to what extent the changes in iron usually referred to as allotropic follow similar laws.

If T is the absolute temperature of the transformation, r the heat change in gm.-cals. per gram, and σ and τ the specific volumes of the allotropes at temperature T, then the change of the temperature of the transition with pressure

$$\frac{dt}{dp} = 24{\cdot}2\frac{T(\sigma - \tau)}{1{,}000\ r}.$$

For the β to γ change in iron, T = 916° C. (1,189° A.) and r is 1·4 gm.-cals.

According to Benedicks‖ the linear change due to the transformation is 0·082 per cent., corresponding to a volume change of 0·25 per cent., whence :—

$$(\sigma - \tau) = {\cdot}0025 \times 0{\cdot}13 = {\cdot}000325$$

$$\therefore \frac{dt}{dp} = 0{\cdot}0067° \text{ C. per atmosphere pressure.}$$

$$= 1{\cdot}02° \text{ C. per ton per sq. in.}$$

* Cohen, *Trans. Far. Soc.*, VII, 1911, p 122. † Ibid., May, 1915. x., p. 231.
‡ Ibid., May, 1915, x., p. 233.
§ Nernst, *Theoretical Chemistry*, 1911, p. 642.
‖ Benedicks, *Jour. Iron and Steel Inst.*, I, 1914, p. 429.

So far as the author is aware there are no experimental determinations available for the checking of this value. Roberts-Austen commenced some work* which led to no definite result with regard to Ar_3 and does not appear to have been continued. It may be said with confidence, however, that the result is of exactly the right order of magnitude, a statement which is strongly confirmed by the cooling curves obtained from a 0·9 per cent. carbon steel under no pressure and under one of 30 tons per sq. in. The pressure has caused the depression of the point $Ar_{3,\ 2,\ 1}$ by about 40° C., and since the absence of any appreciable volume change at Ar_2 means that the pressure is without influence on the temperature at which this change occurs, the exact correspondence of the observed fall with that calculated for Ar_3 is the more interesting.

Tammann† has made the same calculation, using earlier and less accurate data. The results obtained were not considered to be in accord with the experimental data.

Attention may now be turned to the effect of dissolved substances, the depression of temperature caused by which is proportional to the number of molecules (in the case of metals, atoms) of the solute added. The author is at present engaged in work intended to investigate the constitution of carbon and special steels from this depression of the allotropic points, but for the present the following table will indicate that the A_3 change-point is governed by laws exactly the same as those holding for others which are undoubtedly allotropic. The figures for the nickel and chrome steels are those of McWilliam and Barnes,‡ and that for tungsten is due to Swinden.§

TABLE I.

Percentage of Dissolved Element.	Temperature of Ar_3.	Depression Ar_3.	Atomic Weight.	Atomic Depression.
	°C.	°C.		°C.
Pure iron	897	—	—	—
0·22 per cent. carbon ...	830	67	12	3,660
1·98 per cent. chromium	785	112	52	2,940
3·05 per cent. nickel ...	728	169	58·7	3,250
3·24 per cent. tungsten ...	845	52	184	2,950
			Mean	3.270

These results, considering the divergent sources of the temperatures of Ar_3, are sufficiently concordant to show that *the temperature of the A_3 change, like every allotropic change, is depressed by an amount proportional to the number of atoms of the dissolved substance.*

CONCLUSIONS.

1. Sudden changes in the directions of one or more curves showing the relationships of the physical properties of iron to temperature indicate with certainty the existence of α, β, γ, and δ iron, with change-points at 768° C.,

* Roberts-Austen, *Jour. Inst. Mech. Engs.*, April, 1893.
† Tammann, *Zeit. f. Anorg Chem.*, p. 126.
‡ McWilliam and Barnes, *Jour. Iron and Steel Inst.*, I, 1911, p. 280 and I, 1910, p. 255.
§ Swinden, ibid., 1907.

900° C. and 1,400° C., while another slight change has been detected magnetically and dilatometrically at about 830° C.

2. The A_3 point in iron, taken as typical of all the changes, is shown to obey the same laws as hold for other acknowledged allotropic transformations.

3. Magnetic evidence is available that the molecule of β iron is Fe_3, of γ iron Fe_2, and of δ iron Fe.

4. A distinct mode of packing of the α, the β, and the γ molecules is indicated crystallographically.

5. Thermally it may be shown that the changes occurring in iron are of the same nature as those which occur in other cases of allotropy in metals, e.g. tin and cadmium, and also as in the case of the change from rhombic to monoclinic sulphur.

The author is therefore strongly of the opinion that the transformations in iron are essentially allotropic. At the same time he dissociates himself entirely from the view that to any of the allotropic forms *per se* is the hardness of hardened steel due. Some of the modifications will dissolve carbon as Fe_3C and some to all intents will not, but in this fact alone does the allotropy of iron bear on the constitution of steel. Whether iron is allotropic or not, it is to the solution of Fe_3C in it that the characteristic properties of hardened steels must be ascribed. The views of Arnold* expressed in 1895 are essentially accepted to-day by the majority of metallographers, and the "hard β iron" to which, according to the "allotropic school" of metallurgists, the strength of hardened steels was due, is dead.

DISCUSSION.

The following communications to the Discussion were read by the Secretary:—

Professor Pierre Weiss (*communicated from Paris*): In his Paper Dr. Oxley refers to the value of magnetic investigations in order to elucidate the different states of iron, and also to the work I have done on this subject. In my older Paper of the year 1907 which is quoted the α, β, γ states of iron and the transition points between them—A_2, A_3—are discussed from the point of view of the molecular field. According to this theory I agree completely with Dr. Oxley, who points out that in the A_2 transformation there is nothing like an allotropic change of state. Indeed, in the case of magnetite, the transition from the strong magnetic to the paramagnetic state and the properties in the range of these two states are explained, in accurate agreement with the facts, by the assumption of the variable orientation of a definite molecule. There is no reason why the same phenomenon should not be of the same non-allotropic character in iron and nickel.

But since the Paper quoted was issued, new accurate measurements have been made by my assistants and myself on the magnetization of iron at different temperatures. It is shown that one point in which I used, in the paper of 1907, the first investigation of Curie, which was alone available at that time, is to be corrected: the constant C is not the same for the β and γ iron, or below and above the A_2 point. These investigations† have shown that the transformations of iron are at least of three kinds. One is the A_2 transformation already mentioned; this has a true physical character. The

* Arnold, *Trans. Inst. Civil Engineers*, 1895.

† See an account in *Revue générale des Sciences*, 1914, p. 12.

second is the $\beta \longrightarrow \gamma$ or A_3 transformation, which presents a discontinuity in the value of the susceptibility, as already shown by Curie.

The third kind of transformation is in relation to the magneton theory. If we represent the reciprocal value of the susceptibility with reference to the temperature, we obtain for the β region of iron two straight lines, the one corresponding to a β_1 iron with 12 magnetons, the other to a β_2 iron with 10 magnetons in the atom. I think, in this latter case, the intra-atomic character (for the most part) of the change appears clearly, and there is no doubt that, according to the definition of Dr. Oxley, this change is not to be called allotropic.

Professor H. le Chatelier (*communicated from Paris*) feared that in giving a new definition to the word "allotropy" as proposed by Dr. A. E. Oxley one would introduce great obscurity into the science. Somebody else would propose another definition no less legitimate in his eyes, and one would soon arrive at a point at which words would lose all their significance. He regretted that the habit, already too frequent in science, was becoming even more general, of replacing the consideration of experimental facts by atomic hypotheses which evade all scientific criticism.

The word "allotropy" has for long been employed in science and applied to a well-determined collection of phenomena. If one wished to define this word, it sufficed to take all the facts coming under this head and examine again their common characteristics. Adopting this point of view, two allotropic states are two clearly defined states of the same composition, presenting the discontinuity emphasized by Mr. Benedicks, but being able to exist together at the same temperature and the same pressure.

If this point of view be admitted, changes of physical state such as fusion and vaporization should be classed with allotropic transformations properly so called; not only the A_3 transformation in iron but equally the A_2 transformation, seeing that it has been abundantly proved that it is progressive within certain limits of temperature, and that it has not been possible to maintain β iron at temperatures at which α iron is stable, any more than it has been possible to maintain at ordinary temperatures a body with properties which it possesses at much higher temperatures.

Professor Frederick Soddy, F.R.S. (*communicated*): I think Dr. Oxley would find some difficulty in defining what he means by the molecule of a solid, e.g. an iron molecule, for though the expression is common enough it seems to have no exact meaning. In a binary compound such as salt, for example, the researches of Professor Bragg and his son, by the X-ray method of elucidating crystalline structure, have shown that any one of either kind of atom can claim any one of a number, six in the case of salt, of the other kind of atom as its partner in the hypothetical molecule NaCl. In fact, though we are all supposed to know what a molecule is, and nothing could be more sharply defined so long as we confine our attention to the gaseous or liquid states, few of us can have really thought much about it, or it would not have needed the X-rays to show that the extension of the molecular theory to the solid state involves an absurdity.

The mean kinetic energy of translation divided by the absolute temperature is the same for all molecules. This is what defines the molecule, as it has come to us through the theory of Avogadro, and its extension to liquids by van't Hoff and others. The finding out of the number and kinds of atoms which possess this constant kinetic energy of translation, and which therefore constitute the molecule, is easy enough for liquids or gases, but is not possible for solids, because the atoms of the solid are anchored, and do not exist in freely moving groups, i.e. molecules, at all. The only meaning

that the term "molecule of a solid substance" conveys to me is—that aggregate of atoms which remains undivided when the solid is liquefied (dissolved or melted) or gasified. That is, you must define the molecule of a solid as that which would be a molecule if it were not solid, but which being solid cannot be a molecule. It is this *reductio ad absurdum* which is reflected in the difficulty of defining allotropy in reference to substances which exist only in the solid condition.

It is true that there is one case, that of solid oxygen and solid ozone, where there is evidence that in one substance the atoms are united primarily in pairs and in the other into groups of three, however these groups are united among themselves. But these seem to be the only allotropes that survive gasification. There is little evidence that sulphur, phosphorus, etc., in their allotropic modifications are strictly analogous, and in the case of the metals there is even less evidence. In the case of iron there are the magnetic properties that might help, and of course the X-ray method is applicable in the determination of the atomic arrangement. But the thermal evolution or absorption would only be of value if it were great. As it is not, it seems a mistake to draw any inference from it. For there are many well-defined chemical compounds, hydrogen sulphide and hydrogen iodide, for example, for which the heat of formation is less than the heat of vaporization of water. It might be safe to conclude that there were rearrangements in the primary atomic groupings if the heat-change were large, but it is certainly not safe to conclude that there are none because the heat-changes are small.

Dr. J. E. Stead, F.R.S. (*communicated from Middlesbrough*) : I welcome Dr. Oxley's views and hypotheses as likely to lead to some universally acceptable definition of allotropy. The bases or foundations of what were regarded sound for defining allotropy are shaken after the scrutiny by the chemical crystallographers. It remains to find out whether the suggested new bases are or are not equally open to doubt. So far as the practical metallurgist is concerned, it does not matter what the changes are termed. Internal physical changes are associated with profound changes in the properties of metals. These changes have generally been regarded as indications of allotropic modification. I for one would very much like Dr. Oxley to explain the breaking up of large crystals of iron into small ones, when they are heated through the Ac_3 range. There must be a profound internal physical breaking down and rebuilding of the crystalline structure, a change which is accompanied by an absorption of heat.

Professor Thomas Turner (*communicated from Birmingham*) : The paper by Dr. Oxley is very suggestive, and the table of latent heats of fusion, when compared with the thermal evolutions accompanying allotropic changes, is striking. Though Dr. Oxley's arguments appear to show that the changes in iron are more allied to change of physical state than to true allotropy, this would not interfere with our ideas that there are three distinct phases in solid iron, and that these phases possess characteristic properties. It is unfortunate that before men began to speak of allotropic iron they did not first settle in a precise manner the preliminary inquiry, "What is allotropy?" Had this been done much discussion might have been saved.

Dr. Cecil H. Desch (*communicated from Glasgow*) : Before it is possible to discuss Dr. Oxley's paper at all usefully, it is necessary to come to some agreement as to what is to be understood by allotropy. It is evident that the author wishes to restrict the term within much narrower limits than those to which chemists are accustomed. Amongst chemists, the tendency

has undoubtedly been in recent years to widen the conception. The work of A. Smith on sulphur and of Smits on phosphorus has shown that two modifications of an element, characterized doubtless by different molecular weights, may coexist in equilibrium over a range of temperature. By applying different rates of cooling, undercooled products may be obtained which are composed of the two modifications in different proportions. This is an experimental fact, and the modifications are distinguished by such obvious differences of properties as those of colour, not to speak of those which demand exact measurement. This condition of things has been called "dynamic allotropy," and it is evidently of very wide occurrence. E. Cohen has even gone so far as to maintain that all the common metals present instances of this condition, and that our ordinary metals are metastable mixtures of different modifications. One may not accept all Professor Cohen's experimental proofs, but the evidence in the cases of phosphorus and sulphur is clear.

Dynamic allotropy may occur over a range of temperature, and the term "allotropy" here is used in a wide sense. Let us confine ourselves therefore to the older and more restricted sense. Professor Honda adopts the definition "an allotropic change is a change in a substance from one phase to another at a definite temperature." Many chemists would, I think, consider this too narrow, but it will answer the present purpose. Tin is certainly allotropic on this definition, for the change from grey to white tin takes place at a definite temperature, and corresponds with an equilibrium between two distinct solid phases. How does iron stand the test? The point A_3 is a definite temperature, as is generally agreed. Further, it seems to the writer that it corresponds clearly with a change from one phase to another. Probably γ and β iron both crystallize in the cubic system (it is not yet proved that they belong to the same class of that system, and the contrary is more probable), but there are important differences between the two modifications. Dr. Stead has rightly laid great stress on the complete recrystallization of iron on passing through the A_3 point, a sign of some profound change in the space lattice. Moreover, γ iron can dissolve carbide to form a homogeneous solid solution, whilst β iron cannot do so. In an equilibrium diagram, the curve which represents the crystallization of β (or α) iron from the solid solution is a boundary between different fields of phase equilibrium, and this curve, produced, cuts the temperature axis at the point A_3. In the sense of the phase rule, the separation of iron from the solid solution is a change involving a new phase. How, then, can we deny the character of a phase change to the transformation $\gamma \longrightarrow \beta$ at A_3? From a purely chemical point of view, it would seem clear that γ iron and the modification into which it changes on passing through Ar_3, whether it be called β or α iron, are distinct phases.

Another point in Dr. Oxley's communication which calls for remark is the comparison of the magnitude of the thermal effects. An error appears to have crept into the tables of thermal values on p. 133, which produces a misleading impression. The latent heats of fusion are expressed in gram-calories per gram of metal, but the thermal evolutions accompanying allotropic and isomeric changes are expressed in gram-calories per gram-molecule or multiple of the gram-molecule. To make the results comparable the values should all be expressed in the same units. The most appropriate is the gram-atom. This involves dividing the value given for oxygen by 6 (the number of atoms involved in the change $2O_3 \longrightarrow 3O_2$) and multiplying the latent heats of fusion by the atomic weights. This gives us for each gram-atom :—

(Allotropic)	Ozone ⟶ oxygen	9,866 gr.-cals.
	Yellow ⟶ red P	21,000 ,, *
(Latent heat)	Bismuth	2,704 ,,
	Cadmium	1,574 ,,
	Lead	1,036 ,,
	Silver	2,373 ,,
	Tin	1,662 ,,
	Zinc	1,830 ,,
	Gallium	1,328 ,,
	Phosphorus	155 ,,

The disproportion is thus much less than is suggested by the author. The heat of transformation of one gram-atom of grey tin into white tin is given by Meyer as 1,133 gr.-cals., a figure which is less than the latent heat of fusion, although this change is undoubtedly allotropic, whatever definition of allotropy may be adopted.

Turning now to the evolution of heat in iron, the value 1·4 gr.-cals. is again given for 1 gram, and should be multiplied by 55·84 to make it comparable with the value for phosphorus. The writer considers, however, that even this value is much too low. It has been arrived at merely from the maximum rise of temperature during the transformation. The true value should include the whole area of the peak on the inverse-rate or the derived differential curve. Perhaps Professor Carpenter or Dr. Rosenhain, from the large scale curves in their possession, could give an estimate of the value. It is generally considered to be about three times as great as the evolution of heat at Ar_2. This has been determined calorimetrically by Meuthen † to be 5·6 gr.-cals. per gram, which is 313 gr.-cals. per gram-atom. Three times this would be 939 gr.-cals., a value approaching that for the transformation of tin. For the separation of 1 gram of α iron from the solid solution of carbide in γ iron Meuthen found 14·1 gr.-cals., or 787 gr.-cals. per gram-atom.

Taking these facts into consideration, together with others which are sure to be adduced by speakers in the discussion, the present writer sees no reason for removing the $\gamma \longrightarrow \alpha$ or $\gamma \longrightarrow \beta$ change from the category of allotropic transformations. At the same time Dr. Oxley's paper is to be welcomed as a most valuable contribution to the physics of steel, especially in regard to the important and baffling magnetic properties. The present criticisms are merely intended to suggest the chemist's point of view, for comparison with that of the physicist.

Mr. A. McCance (*communicated from Glasgow*) : Much of the confusion which has clouded the discussion of the nature of the A_2 and A_3 points in pure iron has arisen, as Dr. Oxley very rightly emphasizes, from the fact that each one has viewed the question from the standpoint of his own definitions. The question can, then, be asked, Is this new definition acceptable to all?—" Each different atomic structure of the molecule is an allotropic modification."

A definition must not be ambiguous, nor in its explication must it demand a belief in any theory, and I am afraid that in both of these respects Dr. Oxley's definition fails. It requires that to the word " different " a special meaning be given which is restricted and which is based on a special interpretation of facts, and no matter how valuable and ingenious the interpretation may be (and Dr. Oxley's interpretation of diamagnetism has both of these qualities),

* Abegg's *Handbuch* gives only 3,700–4,200 gr.-cals.
† A. Meuthen, *Ferrum*, 1912, **10**, p. 1.

the definition is bound up with the theory and, subject to endless modification, is no longer a fixed point in our knowledge.

Even the word "molecule" is fast losing its significance for crystalline materials, and is being replaced by the crystalline unit, or the minimum number of atoms in space which can define the symmetry of the crystalline form which an aggregate of such atoms possesses; and underlying all modern work is the insistence on this idea, that with any chemical substance the physical properties are determined absolutely by the temperature and by the arrangement of the atoms in space—that is, by the crystalline form. Could a greater difference be imagined than is evident in the properties of diamond and graphite? Yet both are made up of carbon atoms only, set out differently in space.

Changes caused by purely thermal effects are continuous, and in a curve connecting temperature with any specific physical property, therefore, a discontinuous change can indicate one thing only (if chemical changes are absent)—that a change in crystalline form has taken place. In every case of allotropy which has been examined carefully the truth of this has been proved. Sulphur crystallizes in the rhombic and monoclinic; tin in the tetragonal and rhombic; yellow phosphorus is cubic, but red phosphorus is hexagonal. And iron is no exception to the rule.

On heating iron to a temperature above the A_3 point there is a fundamental change in the size of the crystal grains which is the basis of all heat treatment of steel. At this temperature the whole crystalline structure is reorganized, and has to build itself up again right from the very beginnings, and for every grain which existed before there are now hundreds of new small grains. If a change in the closeness of the packing was all that was required, surely the atoms or molecules which make up the grain could expand or contract into their new positions without altering the configuration of the boundaries of the grain. But the new structure cannot be impressed on the old structure in this way; it has to be built up afresh from new centres, and in my opinion this is indubitable proof of a difference in crystalline symmetry. Although it has been asserted that alpha and gamma iron both belong to the cubic system, the evidence offered in support of this would equally apply if either belonged to the tetragonal or rhombic form with axial ratios which did not differ greatly from unity; beta iron, of course, is only non-magnetic alpha iron, and must possess the same crystalline form as alpha.

On this view I have calculated the course of the A_3 curve in steels with increasing carbon content, and the result, which agrees well with thermal change-point data, shows that this curve is continuous without a break where the A_2 and A_3 merge, down to a eutectoid composition of 0·85 per cent. carbon.

It is scarcely an argument against allotropy in metals to compare their latent heat of fusion with the heat-change associated with certain non-metallic transformations, since it is a fact well known that all thermal measurements for metals give decidedly lower values than for non-metals (i.e. specific heat and thermal resistivity), while for strict comparison the latent heat of the metals should have been given in calories per gram-molecule. If the heat liberated at the A_3 point in iron be compared with the thermal effect which is associated with definite crystalline changes taking place in quartz at about 570 and 900, it will be seen that the order of magnitude is the same, so that this line of argument rather confirms the existence of allotropy than otherwise.

So in seeking for a definition let us not neglect the obvious evidence and, keeping the derivation in mind, let an allotropic change be defined as a

change in crystalline symmetry. Other evidence will be admissible, but with the crystalline structure will rest the final decision.

Mr. T. G. Elliot (*communicated from Sheffield*): 1. With reference to his conclusions that the molecules of crystalline and of liquid substances are in a distorted state, Dr. Oxley speaks of the necessity of withdrawing the restraining forces in order to judge between supposed cases of allotropy. How are these restraining forces to be withdrawn? According to Dr. Oxley these restraining forces are present, though of different magnitude, in both solid and liquid substances. How will the mass be built up when these restraining forces are withdrawn? Dr. Oxley's test of allotropy would seem to demand a hypothetical condition in the material to be tested.

2. Again, it is difficult to see how perfect crystals can be built up of distorted molecules. Dr. Oxley states that according to Weiss the iron molecule consists of two atoms in the temperature intervals of stability of the beta and gamma forms.

3. Nevertheless, Weiss, in his recent paper before the British Association on "New Views on Magnetism," states that beta iron is probably Fe_3, gamma iron Fe_2, and delta iron Fe_1, and that there are two beta irons.

4. If Weiss's most recent statement is correct, it conclusively proves that iron is allotropic according to Dr. Oxley's definition.

Professor E. D. Campbell (*communicated from the University of Michigan, U.S.A.*): Dr. Oxley has pointed out that from the viewpoint of a physicist, considering the energy changes only in the A_3 transformation, there is room to question whether the A_3 change is, in reality, an allotropic one. While we have no satisfactory experimental method for directly determining the molecular weight of iron in the solid condition, to say nothing of any means of determining the atomic arrangement within the molecule, we have reasonably accurate methods for determining the concentration of solutes, especially carbides in solid solution. It has been well known for years that above the A_3 transformation the solvent power of iron, especially for carbides, is at least ten times as great as it is when the iron has cooled slowly through the transformation range. If the concentration of carbides in solid solution were plotted as ordinates and temperatures as abscissæ there would be found an abrupt rise in the curve of solubilities on passing above the A_3 point—that is, mathematical discontinuity and the necessity of employing two ordinates, one to express the solubility of carbides below the A_3 point, and the other to express the solubility of carbides above this latter transformation. Viewed, therefore, from the chemist's standpoint, it is difficult to understand how such a marked change in properties without change of state as that which iron undergoes at the A_3 transformation can be considered as anything other than an allotropic one. Certainly the change in solvent power which must be connected with some change in molecular constitution is so abrupt and of such magnitude as to produce, when plotted, mathematical discontinuity, i.e. two ordinates for the same abscissa, thus complying with the criterion as laid down by Benedicks, which, as Dr. Oxley says, "is admirable from a theoretical point of view."

The subject was then thrown open for general discussion.

The President, who opened the Discussion at the meeting, said that the subject was of paramount importance at the present time, for upon it depended our power of hardening the steel required for war material, which so infinitely concerned us now. We had still a lot to learn about the alloys of iron. For instance, Professor Carpenter and he had found that many of

these alloys at the temperature of liquid air attained a tensile strength of 160 tons per sq. in. When the Government took a more practical interest in research, rapid progress would be made. The Society was greatly indebted to Dr. Oxley for the brilliant way in which he had presented his views.

Professor H. C. H. Carpenter : I should like to associate myself with the complimentary remarks of the President. As the author points out, in recent years research work has tended to bring metallurgists more and more into line as regards the question of the A_2 inversion. The old view was that both A_2 and A_3 were points of allotropic change. An increasing number of workers are coming to the view that the transformations are different, and that the A_2 inversion is not allotropic, using the word in the old sense. It is extremely interesting to find the A_3 point challenged in the same way. Personally, I am one of those who regarded γ iron as firmly established. The view of most of us has been that above 900° C. the γ phase exists, and below it another, viz. *a*. As Dr. Oxley points out, it is difficult to define allotropy. I think it is at the moment impossible to do so. He points out the difficulty of testing Benedicks' theory ; I agree.

Oxley says, "Each different atomic structure of the molecule is an allotropic modification." Also, "We must distinguish between the forces holding the molecules in position in the crystalline structure and those holding the atoms together in the molecule." It is clear, therefore, that he holds the view that the iron molecule contains more than one atom. Now does it ? I am here thinking of Bragg's work on X-rays and crystalline structure. Oxley says we have the atom, the molecule, and the crystal ; Bragg shows that we may have the atom and then, as the next step, the crystal. He concludes that the crystal is built up of atoms and not molecules. This is interesting, because the metals, such as Hg, Zn, and Cd, whose molecular weights can be determined, are monatomic. It is, however, difficult to determine the molecular weights of solid substances, so that Bragg's method is important as it appears to give us a method of determining this in the case of crystalline substances. He has, as I understand, come to the conclusion that the crystals of copper are built up of atoms. I know that he is anxious to get hold of some good crystals of iron, and if Sir Robert Hadfield can furnish him with some, this test could be carried out. According to Weiss the iron molecule contains more than one atom, so that it is very important that experiments of this kind should be made.

Oxley also quotes Barlow and Pope, and says that iron always crystallizes in the cubic system. I should like to point out that above 900° C. iron often crystallizes in octahedral forms, but that below this temperature it always crystallizes in cubes. The types of crystallization above and below the A_3 point are therefore different.

Oxley says, "If there is no abrupt change of the atomic constitution of the iron molecule, then changes of the properties of pure iron such as occur at A_3 must be ascribed to a change of crystalline grouping of the molecules. This change must be of such a nature that the crystalline symmetry is not affected on passing A_3 ; a change of the closeness of packing of the molecules is all that is required" ; also, "The thermal energy evolved on cooling through A_3 is just the heat of transformation from a more open to a closer packed cubic system." He is no doubt familiar with the work of Le Chatelier, Charpy, and Benedicks, on the volume changes at the A_3 point. Benedicks has shown that there is a linear expansion on passing through Ar_3 of 0·082 per cent. This does not seem to me to fit in with the view that the change is from a more open to a closer packed system.

I will now show a few slides illustrating the crystallographic changes at the A_3 inversion which Dr. Stead and I demonstrated two years ago with exceptionally pure iron, prepared electrolytically.

Description of Slides.

The iron was in the form of strip about 0·01 of an inch in thickness.

Fig. 1 shows its structure magnified 1·76 times after being kept 72 hours at 890° C., i.e. just below the Ac_3 inversion. The crystals are small and equi-axed.

Fig. 2 shows the structure after one hour at 910° C. At the one end you will notice that the crystals are very much the same as in No. 1 ; but at the other a remarkable change is evident. For the most part the crystals are extremely small, but here and there very large new crystals have been formed. On this specimen we have the complete history of the structural change at the A_3 inversion—a change which is accomplished within a very narrow limit of temperature. We have—

(*a*) the original small crystals;
(*b*) a few of the new very large crystals ; and
(*c*) the very minute crystals representing the iron in the transition stage between (*a*) and (*b*).

What the temperature variation on the specimen was I do not know, but I do not think it was more than 2° C.

Fig. 3 represents the structure after one hour at 915° C., when the change is complete. The iron is now a mass of very large crystals.

Fig. 4 shows on one and the same specimen the two types of crystallization alluded to. This result was obtained by placing the strip in a furnace heated to just above the Ac_3 point and removing it before its central area had reached that temperature.

Besides these very remarkable crystalline changes, the tensile strength decreases enormously, as was shown by Benedicks in 1914, using the same strip of iron.

I consider that the investigation of these properties of iron indicates that a profound change occurs at the A_3 point, and that Oxley's theory in no way accounts for them.

With regard to the thermal data, I notice that Oxley has quoted the figures of Arnold, but as the latter gives 854° for the Ar_3 inversion, which is 44° too low, the rate of cooling must have been much too rapid for accurate thermal measurements. What has to be measured is the total heat energy of the change. In any case the comparison with latent heats of fusion given seems to me to be beside the mark, as we are not dealing with a change of state of that kind. Also I do not think it fair to suggest, as Dr. Oxley has done, that the thermal evolutions accompanying allotropic or isomeric change are all strongly exothermic. Certainly there are well-known instances of isomeric change where the thermal evolutions are very much smaller than those he has quoted.

Dr. J. A. Harker, F.R.S., said that the Paper had been very interesting to one who knew extremely little of the subject. He expressed his astonishment that the thermal constants of iron were practically unknown, when they were of so much importance to metallurgists. It ought to be possible to devise a calorimeter in which iron is heated up to above its melting-point, and the quantities of heat used up at various stages determined.

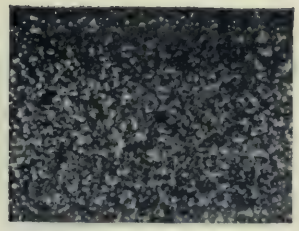


FIG. 1.

FIG. 2.

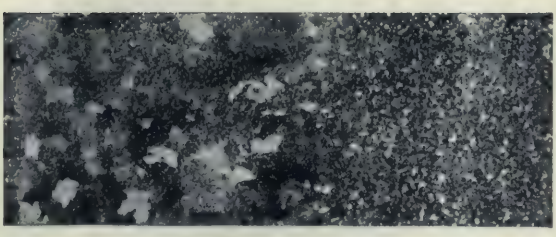
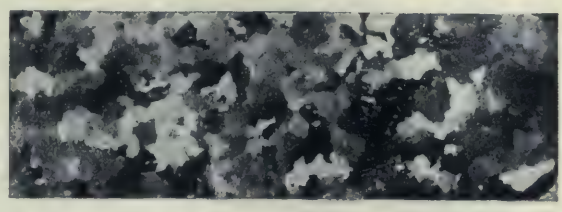


FIG. 3.



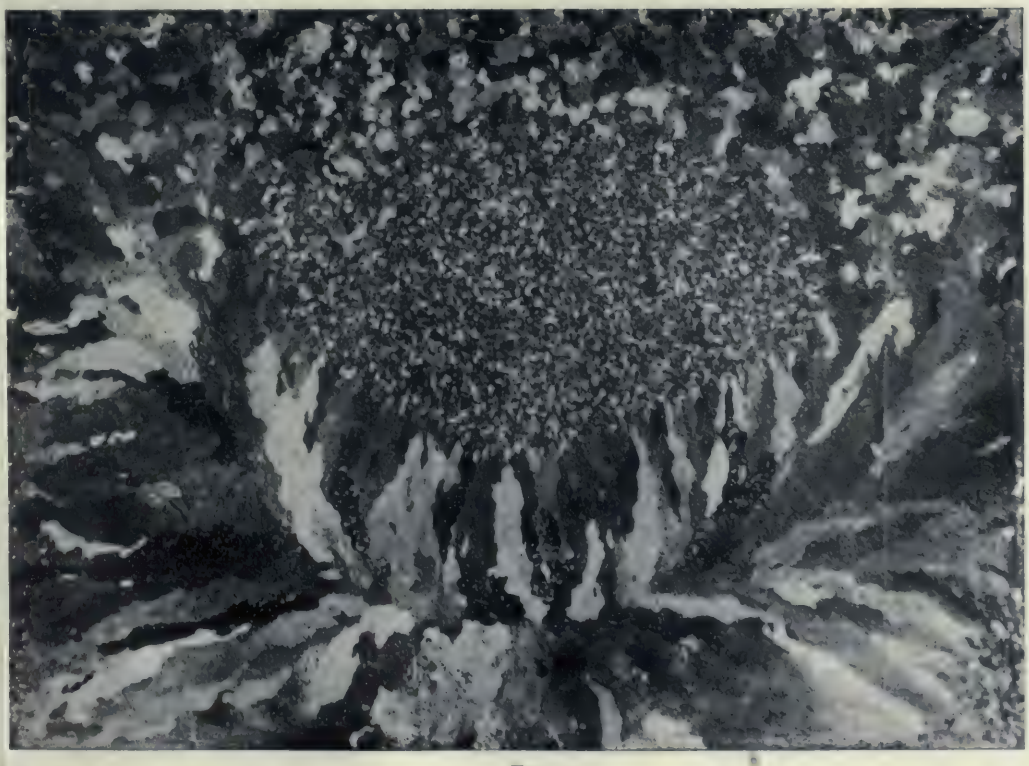


FIG. 4.

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The President said he would be pleased to defray the expenses of the determination of the physical constants of iron if the National Physical Laboratory would undertake the work.

Professor J. W. Nicholson: I wish to echo the remarks of the previous speakers and express the pleasure which I have experienced in listening to Dr. Oxley's Paper. Speaking purely as a physicist, I should like to mention one or two points that have struck me.

The work of Weiss seems to be fundamentally important in connection with the physical basis of phenomena of this kind, for magnetic phenomena appear to be one of the main sources of our information regarding atoms.

Dr. Oxley mentions ferrous chloride and iron carbonyl, one paramagnetic and the other diamagnetic, and introduces the idea of atomic allotropy. This is the really new feature in Oxley's Paper, and it is a feature which promises to lead to valuable results, and which at least can suggest new lines of work.

There are many varieties of allotropy, and we must subdivide them into different groups. It seems to me that atomic allotropy is a form we will have to consider carefully.

I was glad that Professor Carpenter introduced Bragg's experiments, because I think we can deduce from them a view favourable to Dr. Oxley. The question of the constitution of the iron molecule comes to the front. In view of Bragg's work it is becoming difficult to have a clear idea of the molecule in a crystalline substance. In a crystal of sodium chloride analysed by the Bragg method, the sodium and the chlorine seem to preserve their identities. It seems rather difficult to prove that the molecule of iron contains only one atom, because the relation between one row of atoms and another may be the same as between a row of sodium atoms and a row of chlorine atoms in a crystal of sodium chloride. We must study the relations of an atom to all the atoms round it. If it does not bear the same relation to all the atoms round it, their distances apart would not be the same all round it. Mathematically there must be equilibrium among the atoms, and always in the same way under the same conditions. Therefore, if there are differences in the relations of surrounding atoms in the crystal, there must be differences in the atoms themselves to account for it; hence atomic allotropy. In the absence of such allotropy, two different crystals do not seem possible.

Dr. Oxley's suggestion is well worth working out; it is quite new, and may manage to solve some of these puzzling phenomena.

Professor Alfred W. Porter, F.R.S.: I wish to make a remark about the first part of the Paper. Dr. Oxley proposes a new definition of allotropy, the application of which would involve removing a molecule out of the influence of restraining forces due to other molecules. Now, a definition is of no use unless it can be applied, and Dr. Oxley does not explain in what manner this application would be made. The only way that I know by which the molecules could be so set free would be by evaporation. Any restraining forces remaining would then be very small. The process, I presume, would consist in evaporating each of the two substances under test and then investigating the vapours to see if they were in any wise different. But in the majority of cases (e.g. iron) the temperature would need to be raised to produce enough vapour for the investigation; and there would be no guarantee that the vapour at the higher temperature would retain any of the molecular characteristics of the solid or liquid from which it had been formed. This doubt might also exist even if the temperature had not needed to be raised. Gaseous ozone is known to be O_3, but this formula probably does not measure the molecular complexity of the liquid. I would like to ask

Dr. Oxley whether he has some other and more reliable way of applying his definition. I may add that he does not himself use it in discussing the properties of pure iron in his Paper, but falls back upon other criteria.

Allotropy, Polymerism, Isomerism, and Polymorphism.

Dr. T. Martin Lowry, F.R.S., wished to protest against the idea that physicists and metallurgists were at liberty to alter the definition of allotropy that had been used by chemists during the greater part of a century. That definition was given by Berzelius in 1841* when he introduced the term "allotropy," to describe "dissimilar states in simple substances." The elements to which the name was first applied were sulphur, carbon, and silicon; two years later phosphorus was added to the list; the case of oxygen and ozone was not used as a type, because at that time and for some years later ozone was only known as an odour and not as a definite substance.

Following Berzelius, chemists have always used the term "allotropy" in the broadest possible sense to cover all the modifications of an element, whether these are due to polymerism, isomerism, or polymorphism. In the case of sulphur, for instance, we have polymerism in the vapour, $S_8 \rightleftharpoons 4S_2$ isomerism in the liquid (soluble and insoluble sulphur are both S_8), and polymorphism in the soluble crystalline solid, which may form rhombic, prismatic, nacreous, or tabular crystals. All of these phenomena are described under the heading of "The Allotropy of Sulphur." A similar broad usage applies in the cases of carbon, phosphorus, tin, antimony, and cadmium.

To exclude from the definition all cases of polymorphism would be both novel and dangerous. It cannot be recognized too clearly that it is a dangerous speculation to assert that the difference between two crystals is "*mere* polymorphism," if this term is used to assert that there is no difference of structure in the molecules of which the crystals are composed. The reality of the risks which are involved is indicated by much of the modern work in chemistry, and especially by the experiments which have proved the abundance of reversible isomeric and polymeric changes, and the ease with which these may be mistaken for "mere" polymorphic changes. A single illustration will suffice to illustrate this point. π-Bromo-nitrocamphor was described in 1896 as existing in polymorphic forms melting at 108°, 126°, and 142° respectively. Examination of the freshly prepared solutions showed that these differed widely in rotatory power, the form melting at 142° being a dextro-rotatory isomeride giving $[\alpha]$ + 188°, whilst the form melting at 108° was a lævo-rotatory compound giving $[\alpha]_D$ — 51°; the third modification was a mixture of the other two. Within a few hours the solutions all became identical in rotatory power, giving $[\alpha]_D$ — 38°. This transient difference of rotatory power was the only indication that the different modifications were composed of isomeric molecules, instead of identical molecules marshalled into dissimilar crystals; if these compounds had been optically inactive, or if they had changed into one another a little more quickly, the isomerism would have remained undisclosed, perhaps permanently. It is no exaggeration to say that scores of cases of supposed "polymorphism" may be suspected of masking labile types of isomerism, but that when isomeric change is rapid the task of converting suspicion into proof becomes almost hopeless. In precisely the same way it may prove to be almost impossible to nail down a case of reversible polymerism, if polymeric change is rapid. Thus one may suspect that the various types of light ice discussed by Tammann and others are built up from identical molecules of trihydrol, H_6O_3, and that the various

* *Jahresbericht*, 1841, **20**, Inorg. Chem., p. 13.

forms of dense ice described by Tammann and by Bridgman are composed of identical molecules of dihydrol, H_4O_2; but it is very difficult to prove this, in view of the fact that no anomalies can be detected in the properties of freshly melted ice. If water were an element instead of a compound, all these modifications would be described as allotropic, and the necessity of discriminating as to the origin of the differences would scarcely arise.

Dr. Oxley's contention that the differences between β and γ iron are not incompatible with "mere" polymorphism would be welcomed by the physical chemists who have accepted the allotropic theory of the nature of steel. The original diagram of Roozeboom suggested that α, β, and γ iron behaved as if they were polymorphic forms of the metal; or that, if differences of molecular structure existed, they were effected rapidly and without very much lag. To assert therefore that the difference between β and γ iron was "not allotropy but polymorphism" was merely to confirm the allotropists in their belief, as chemists would read this phrase as meaning "not allotropy, but allotropy."

The idea that the allotropic theory could be killed by altering the meaning of the word "allotropy" was a reflection upon metallurgists, who had surely not divided themselves into two schools in order to discuss the meaning of a name which was defined sufficiently well over seventy years ago. Some clear statement of the difference between these two schools would be welcomed by many who had not followed their discussions in detail, but who were left at the close of the evening wondering whether the whole dispute was after all merely about the meaning of a familiar word.

Dr. Oxley's thermal data are quite unconvincing. He has selected cases in which the thermal changes are large, but might equally well have chosen those in which they are small. Scores of cases are known in which isomerides differ so little from one another in stability that a mixture in evenly balanced proportions is formed as soon as they are melted. In such cases the thermal changes involved must be very small, and perhaps negligible. A similar statement might be made in reference to certain cases of polymerism.

A final word may be added in reference to the crystallography of iron. There are not less than five cubic systems, all giving rise to cubes and to octahedral or tetrahedral forms. Even in the holohedral cubic system two types of structure may be distinguished. It is therefore quite possible for α, β, and γ iron to crystallize all of them in octahedra or cubes and yet to exhibit in the marshalling of their particles different types of symmetry, which might be revealed by etching, or by the examination of minute facets on the corners and edges of the crystals.

Dr. E. K. Rideal: Before discussing the question of the atomicity of the molecule of iron, or the allotropic nature of different modifications of iron, we should wait until Bragg has examined crystals of iron with the X-ray spectrometer. Regarding the two cubic modifications of iron, Partington measured the vapour pressure of hydrated copper sulphate crystals by passing air over them, and obtained results different from those obtained by the static method. These differences might be explained possibly by reference to a labile form of orientation in the space lattices of the crystal. Will it be possible to do similar work with iron at various temperatures? In any case we might correlate the vapour pressures of salts of iron with their magnetic properties. Dr. Oxley might have included other thermal data in his table; for instance, the two different aceto-acetic esters, in which the thermal changes are practically nil. In regard to Dr. Oxley's suggestion that in a space lattice certain atoms must bear a peculiar relationship to certain

and not to all other atoms, otherwise sodium chloride might break down to sodium and chlorine or benzene to carbon and hydrogen, it might be noted that in atoms of the same chemical nature and in substances which do conduct, but not electrolytically, the union is much more labile and a special relationship need not necessarily be insisted upon to provide an adequate explanation of the phenomena observed.

Mr. J. R. Partington : I should like to mention that in addition to Bragg's X-ray method there is a second method of finding the atomicity of a solid element, namely by measurement of its specific heats over a range of temperature. This method has been worked out especially by Nernst, whose experiments are in striking agreement with the new theory of energy-quanta put forward by Planck, Einstein, and Debye. It was found that many metals in the solid state are monatomic, and the idea that the molecules of solids are generally very complex can no longer be entertained. The solid form of a substance may be simpler than the liquid form. It is interesting to note that Nernst's experiments led him, about the same time as, but independently of, Professor Bragg, to the conclusion that the diamond is monatomic, whereas the idea that it possessed a very complex constitution had previously been held. An account of Nernst's work will be found in his book, *The Theory of the Solid State*, London University Press, 1914.

Dr. H. Borns : I hope Dr. Oxley will embody his introductory remarks in his Paper; they certainly make his standpoint clearer. The question I wished to put has partly been answered by the communication from Professor Weiss. Dr. Oxley says that the iron molecule consists, according to Weiss, of two atoms throughout the range of the β and γ forms, and he refers to early papers of Weiss from 1907. But at the Manchester meeting of the British Association, a few weeks ago, Weiss put a diagram on the blackboard in which he distinguished two β irons between 775° and 900°, β_1 with 10 and β_2 with 12 magnetons, γ iron with about 40 magnetons between 900° and 1,400°, and δ iron with 20 magnetons above 1,400°. He also said that β iron was possibly Fe_3, γ iron Fe_2, and δ iron Fe_1. That seems incompatible with what Dr. Oxley stated in his printed Paper, and the additional remarks of Dr. Oxley do not help us over this difficulty.

Dr. G. K. Burgess wrote (*communicated from the Bureau of Standards, Washington, November* 16, 1915) that he had said so much recently on the subject of the transformations in iron, he felt diffident about contributing to the discussion of Dr. Oxley's most interesting paper ; but lest silence should be construed as acquiescence in Dr. Oxley's very ingenious hypothesis concerning allotropy, he would venture to state as follows :—

What is desired is a definition of allotropy which may readily be applied without ambiguity, which would dissipate the confusion now existing, and which may readily be tested experimentally. Dr. Burgess could not agree that, in the light of our present knowledge as distinct from hypothesis, the definition advocated by Dr. Oxley met any of these requirements satisfactorily. If accepted in the form as presented, it apparently removed iron entirely from the allotropic field. It would then be necessary to frame a new set of definitions and terms to describe the A_2 and A_3 transformations in iron, which cannot be deprived of their physical existence by any hypotheses based on allotropy or non-allotropy. It seemed to Dr. Burgess more convenient to so frame the definition of allotropy as to allow the inclusion of both A_2 and A_3.

There are also in Dr. Oxley's presentation of his hypothesis concerning allotropy several statements which might be questioned, and which have probably been dealt with by others, such as assuming Weiss's atomic numbers

as facts, and calling β iron ferromagnetic, and the misleading relations of heats of formation and of transformation.

There are infinite possibilities in framing definitions of allotropy, and the discussion concerning iron is probably so inordinately acute because one has usually in mind the effect of the definition on the iron-carbon alloys.

Dr. A. E. Oxley (*reply partly communicated, January* 17, 1916): Dr. Lowry has referred me back to Berzelius and the definition of allotropy given by this distinguished chemist in 1841. On a point of historical interest I should like to point out that the discoverer of the rhombic and monoclinic forms of sulphur was Mitscherlich, who sent an account of them to the Berlin Academy in 1826. Mitscherlich, however, described sulphur as di-morphous. The term "polymorphism" is carefully distinguished from the term "allotropy" in Professor Tutton's *Crystals* (an expanded account of his address delivered at the Winnipeg meeting of the British Association). Tutton * points out that the transition from rhombic to monoclinic sulphur is not of the same kind as that from diamond to amorphous carbon, or from yellow to red phosphorus. In his opinion, the two latter changes probably involve a rebuilding of the atomic structure of the molecule, whereas the sulphur transition is merely a change of molecular grouping. It is interesting to note that the large thermal energy accompanying the allotropic transformation of carbon, as compared with that associated with the transformation in sulphur, is also used by Professor Tutton as an indication of processes of a totally different nature.

Dr. Lowry seems willing to accept the definition of allotropy given by Berzelius, i.e. he defines allotropic modifications as "dissimilar states in simple substances." I should like to ask Dr. Lowry what he understands by the word "dissimilar" used in this connection. Mr. McCance has criticized the use of the word "different" in the definition I used in my Paper, although I took special care to qualify this word, and, in my opinion, the qualified meaning is quite definite. But Dr. Lowry is satisfied by the word "dissimilar," which I venture to say would not be considered sufficiently precise by Mr. McCance. Is not a dissimilar state produced for every temperature and pressure? In that case the question is not "What is allotropy?" but "What is allotropy not?"

If Dr. Lowry can isolate the β and γ forms of iron and can show that the molecules of these so-called allotropic forms differ in some one respect, e.g. if he could apply any test as crucial as that of the rotatory power test which he quotes, I am willing to submit, but not until he has brought forward such evidence. Sir Robert Hadfield has pointed out in his opening address that the α, β, and γ forms of iron have never been isolated and tested.

With regard to my conception of polymorphism, I consider that at the absolute zero the molecules of a crystalline grain will all be mutually bound together, so that the whole grain forms one enormous physical complex. This complexity gradually breaks down as the temperature is raised, but while the crystalline state remains the molecules are bound more or less closely to their neighbours throughout the crystal, and their vibrations depend upon their mutual forces (cf. Debye's theory of specific heats and the connection between specific heat and the elastic constants of a substance). Such a continuous variation of polymorphism would, on Dr. Lowry's view, imply an unlimited number of allotropic modifications ("dissimilar states"). If Dr. Lowry's definition of allotropy is accepted there is no possibility of killing the allotropic theory—to quote his words, it is immortal.

* *Crystals*, pp. 135–9.

Professor Carpenter says: "It is clear that he holds the view that the iron molecule contains more than one atom" (p. 147). This is in reference to my remark, "We must distinguish between the forces holding the molecules in position in the crystalline structure and those holding the atoms together in the molecule." On referring to my Paper (p. 131), it will be found that this statement was made in connection with matter in general. All that I wish to show is that the atomic complexity of the iron molecule is the *same* on either side of A_3, and (as stated at the meeting) the argument given holds equally well if the iron molecule contains one atom only. Hence this work is not necessarily inconsistent with Professor Bragg's theory of crystal structure. (See also the remarks of Professor Nicholson, p. 149, and the reply to Professor Weiss's communication below.)

The question of a contraction on heating through the A_3 point is further illustrated by recent work by S. R. Williams * on the magnetization of iron spheroids. An increase of the distance between the spheroids in the direction of induced magnetization resulted in a falling off of induced magnetization, but increase of distance in the perpendicular directions produced no measurable effect on the latter quantity. Thus clearly we could get augmented magnetic effect due to a closer approach of the iron molecules in the direction of spontaneous magnetization, while no appreciable magnetic change would be produced by separations in the perpendicular directions, and these latter separations may be so large as to produce a volume expansion. These effects would explain an increase of volume or length on cooling through A_3, accompanied by increase of magnetization in a *mass* of iron crystals possessing all possible orientations. It may be of interest to note that silver iodide (hexagonal) expands along the axis while contracting in perpendicular directions.

With regard to the interesting facts brought forward by Professor Carpenter dealing with the importance of the size of crystalline grains in pure iron, I admit there are many points which my theory will not account for without further development. But let us examine the results of Professor Carpenter as shown by the photographs. On No. 2 slide he showed us three types of crystals (*a*), the original small crystals as shown in No. 1 for the specimen at 890° C., (*b*) a few of the new very large crystals, and (*c*) the very minute crystals representing the iron in the transition stage between (*a*) and (*b*). Professor Carpenter says that "Oxley's theory in no way accounts for them." Neither does the allotropic theory. If the difference of size of the crystalline grains is determined by allotropy, then what is implied by the existence of the type (*c*), which Professor Carpenter says consists of very minute crystals *representing iron in the transition stage between types* (*a*) *and* (*b*)? If his argument is that difference of size of crystalline grain indicates allotropy—and this is the only interpretation to be put upon it—then surely the existence of the type (*c*) implies a new allotrope which exists in the transition from allotropic β to allotropic γ iron. This intermediate allotrope is not considered to be sufficiently important, however, to be classed along with the other so-called allotropic modifications. The very existence of the type of grain (*c*) suggests a continuity in the transition at A_3.

Change of state from one crystalline form to another is not, according to Professor Carpenter, of the same kind as that of crystallization from a liquid. It cannot be denied, however, that in each case the process consists in a re-assemblage of the molecules, and any difference between the two is only one of extent, not of kind.

* *Phys. Rev.*, vol. 35, 1912.

The question of the abstraction of the restraining forces mentioned on pp. 129 and 130, which has been criticized by Professor Porter, is a purely theoretical point. Suppose we draw boundaries round the molecules of the crystalline medium. The molecules will be slightly distorted by the forces exerted on them by their neighbours, but still we should be able to assign to them a definite (though distorted) shape, determined by the internal atomic configuration. If we imagine the restraining forces abstracted, the distortion will disappear, but if the number of atoms and their relative arrangement remain the same, then the atomic structure of the molecule will be the same for the liquid and crystalline states and allotropy will be absent. In the same way, if the α, β, and γ states are composed of molecules having the same atomic arrangement, then although the molecular distortion may be different in each, yet the iron will not show allotropy in the sense used in the present Paper.

Professor Weiss and Dr. Borns have justifiably criticized the magnetic treatment I have given and which is dependent upon the earlier work of Professor Weiss. In a later research,* *using more recent data and assuming that each iron atom possesses an integral number of magnetons*, Professor Weiss shows that the transition β to γ at A_3 may be represented by a change from a tri-atomic to a di-atomic molecule. If, however, the magnetic particle of the β state consists of three molecules (i.e. each molecule is bound to two others, one in front and one behind, in the direction of its magnetic axis, all the molecules of a crystal grain being thus mutually held together) and that of the γ state of two molecules, the magneton theory will still hold, but now the number of atoms in a molecule of each state is the same, viz. one. This would appear to conform with recent X-ray determinations of the structure of crystals. (See also the reply to Professor Carpenter above.) The view that the β state is composed of molecules mutually bound together in this way seems more probable than the one which attributes to β iron a tri-atomic molecule and to γ iron a di-atomic molecule, for γ iron possesses (according to Professor Weiss) more magnetons per molecule than β iron does, and, therefore, unless we suppose that the molecules of the β state are so bound together that one cannot rotate without dragging along its neighbours, it is difficult to account for the rapid increase of susceptibility which occurs on cooling through A_3.

There is one point which I would like to discuss in connection with the β_1 and β_2 states recognized by Professor Weiss. The transition β_1 to β_2 is of the kind which I have called "atomic allotropy" in the concluding remarks of my Paper.† Professor Honda considers that the β_2 state is merely a transition state between β and γ iron.‡ The question as to whether there is a definite discontinuity at A_3 does not admit, in my opinion, of an experimental solution, at least with the means at present at our disposal. (Cf. the recent curves given by Honda.§ These curves show distinct variations of slope in the β_2 region and also considerable variations of rounding off close to the A_3 point.) Also the fact that Weiss has found a definite Curie constant for β_2 iron, which constant is the parameter of the hyperbola connecting susceptibility with absolute temperature, shows that the magnetization curve for the transition β_1 to γ iron is not a true discontinuity in the sense defined by Benedicks, viz. two ordinates for the same abscissa. I agree with Professor Weiss, who says that at A_2 there is nothing like an allotropic change, and it

* *Journ. de Phys.*, vol. i., p. 965, 1911.
† See also *Nature*, vol. 96, p. 272, 1915.
‡ *Science Reports*, Tokio, vol. iv., No. 3, p. 193, 1915.
§ *Journ. Iron and Steel Inst.*, 1915.

appears further that the change at A_3 will probably be found to be allotropic only in the sense of a change of the electric and magnetic structures within the atom, as Professor Weiss's latest results indicate.

At the request of Dr. Borns I have embodied in my Paper the introductory remarks read before the discussion.

In reply to Dr. Desch's communication, I agree that β and γ iron may be distinct phases, but they do not appear to be allotropic in the sense of an alteration of the atomic structure of the iron molecule (see the communication from Professor Turner, p. 142). The numbers which I have given for comparison from the thermal point of view are correct, but it would have been better if they had been referred to the gram-molecule and not to the gram. Dr. Desch has used the gram-atom, but it is really a property of the molecule which we are considering. The thermal energy accompanying allotropic change is still large compared with that evolved on crystallization, when we use the gram-molecule as unit, although the comparison is not so striking. But on further examination it is seen that we ought not to expect the difference of the thermal effects of the two types of transformation to be more than the modified numbers show, since the difference depends only upon the closer proximity of the atoms in the molecules as compared with that of the molecules to one another. The large value of the intermolecular forces within a crystalline structure is shown by the high value of crystalline rigidity.* Further, there is the important question as to the exothermic or endothermic nature of the transition. On cooling through A_3, γ iron passes into β iron with a thermal evolution represented by 1·4 cal./gram. Let us assume that this transition is due to a change from di-atomic γ iron to tri-atomic β iron :—

$$3 . Fe_2 \longrightarrow 2 . Fe_3 + 470 \text{ cal.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the oxygen to ozone transformation, however,

$$3 . O_2 \longrightarrow 2 . O_3 - 57{,}600 \text{ cal.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We certainly, therefore, cannot regard the transition at A_3 as of the same nature as that from oxygen to ozone. Further, if the A_3 transition is correctly represented by (1), to what molecular change are we to ascribe the transformation at A_2 (which has a smaller thermal value than that at A_3) if, as many metallurgists believe, the transition at A_2 is allotropic?

Mr. McCance refers to "crystalline structure" as a basis for deciding for or against allotropy. He quotes sulphur as rhombic and monoclinic, tin as tetragonal and rhombic, yellow phosphorus as cubic, red phosphorus as hexagonal, and further states that "iron is no exception to the rule." Dr. Desch has pointed out that γ and β iron both crystallize in the cubic system, but belong probably to different *classes* of that system. If allotropy is determined by difference of crystalline symmetry, we are again up against that difficulty of words which Mr. McCance has been so anxious to point out in regard to my use of the word "different." What does Mr. McCance mean by "difference of crystalline form"? Does he mean to include various types and habits (or classes, as we may call them) of the same system, such as are believed to occur in iron, along with the obviously different symmetries he has mentioned in the cases of tin, sulphur, and phosphorus? The very words used by Mr. McCance in criticism of my use of the word "different," which he says is subject to "endless modification," apply equally to his conception of crystalline symmetry. Mr. McCance believes that there is a profound change of crystalline form in the transition γ to β iron, and therefore A_3

* Cf. *Phil. Trans.*, A, vol. 215, p. 79, 1915.

is an allotropic change-point. Further, he says that "β iron, of course, is only non-magnetic α iron, and must possess the same crystalline form as α." Therefore A_2 cannot be an allotropic change-point. In view of the fact that Dr. Desch points out that the thermal evolution at A_2 is as much as one-third that at A_3, to what are we to ascribe this thermal evolution at A_2? A_2 is not allotropic because there is no change of crystalline form; A_3 is allotropic because there is probably a change of class in the cubic system, irrespective of the extent of thermal evolutions which are comparable in the two cases. On the other hand, Dr. Burgess points out that my definition of allotropy would remove iron from the allotropic field, and considers it more convenient to frame the definition of allotropy so as to include both A_2 and A_3. In the light of the recent researches of Professor Honda,* such a course seems quite out of the question; and, indeed, Professor Honda has shown, assuming A_3 to be an allotropic change-point, that the transition of A_2 cannot be regarded as allotropic. If we adopt Dr. Burgess's suggestion, the widely different phenomena accompanying the changes at A_2 and A_3 would determine such a wide conception of the term "allotropy" that every change in matter would have to be described as allotropic, and the term would accordingly become useless (see also the reply to Dr. Lowry above).

In reply to M. Le Chatelier, I say that the definition of allotropy given in my Paper is not a new one; it is merely a narrower conception of the term, which is not inconsistent with the type of the oxygen to ozone transformation, which chemists, metallurgists, and physicists all admit as allotropic.

M. Le Chatelier (cf. Dr. Burgess's remarks) says that the A_2 transformation, too, is allotropic, seeing that it has been abundantly proved that it is progressive within certain limits of temperature, and that it has not been possible to maintain β iron at temperatures at which α iron is stable, any more than it has been possible to maintain at ordinary temperatures a body with properties which it possesses at much higher temperatures. Now, the dissociation in liquids is also progressive within certain limits of temperature, and it is not possible to maintain the state existing at one temperature at a much lower temperature. Therefore mere physical grouping of molecules determines allotropic state and the number of possible allotropic states becomes unlimited. It is with the desire to avoid this obscurity that the narrower definition based on the oxygen to ozone transformation—a transformation which is accepted by *all* as allotropic—has been adopted.

I quite agree with Professor Turner that the so-called α, β, and γ states of iron are different phases. So also are ice, water, and steam. But they are not allotropic states, since they are composed, so far as we know, of similar molecules in each case, the molecules being grouped into more or less complex aggregates characterizing the different states or phases. This aggregation is of a physical nature and does not determine allotropy.

The points raised by Mr. T. G. Elliot have all been fully dealt with in the replies to other speakers, with the exception of the one concerning distorted molecules. He states, "Again, it is difficult to see how perfect crystals can be built up of distorted molecules." The fact that the molecules of a crystalline structure are so rigidly held together implies the existence of very large controlling forces between the molecules, and these forces must distort the molecules of all crystalline media. Each molecule must have a definite (probably irregular) shape, determined by the distribution of the forces due to the electric and magnetic elements contained within its atoms, and if all the

* "On the Nature of the A_2 Transformation in Pure Iron," *Science Reports*, Tokio, vol. iv., No. 3, p. 169, 1915. See also "On a Magnetic Study of the A_3 Transformation in Pure Iron," ibid., p. 261.

molecules are *similarly* distorted by the forces due to surrounding molecules, there is no reason whatever why the crystalline structure resulting should not be of the highest degree of symmetry; for the distorted shape of each molecule is probably no more irregular than that corresponding to the free molecule.

In connection with the remarks of Dr. E. K. Rideal on the recent X-ray determinations of crystal structure, the views of Professor J. W. Nicholson given above (p. 149) are interesting. With regard to the later remarks of Dr. Rideal, the difficulty I mentioned was one of the isomers benzene and dipropargyl. If there is no distinction of the groupings of the carbon and hydrogen atoms in the crystalline forms of these substances, how is it that on fusion we do not get a mixture of the two isomers? That we do not get such a mixture is conclusive proof that in the case of these substances, at least, the molecules within the crystalline structure are different in the two compounds. In other words, we can say which carbon and hydrogen atoms form a given molecule in each case, and we can also in imagination draw a boundary round the molecule.

Professor W. H. and Mr. W. L. Bragg have shown the difficulty of defining the molecules of the crystals they have examined, although in many cases this is possible. But to determine by their method whether, in an iron crystal, any atom has a *special* relation to one of those surrounding it, would be impossible. The optical effects which they investigate are determined only by the nucleus or core of the atom, and the outer arrangements of the atom, determining its allotropic forms (atomic allotropy), might differ considerably without being capable of detection except perhaps by their magnetic properties. If, therefore, by the X-ray method, we cannot exclude the possibility of the existence of magnetic connections between the atoms of a molecule, the X-ray method alone does not suffice to show that the extension of the molecular theory to the crystalline state is not valid. Hence the remarks of Professor Soddy (p. 141) as to the absurdity of such an extension may need qualification.

The point raised by Mr. F. C. Thompson in connection with the magnetic change at A_3 has already been considered in my reply to Professor Weiss and Dr. Borns. Mr. Thompson next refers to Nernst's definition of allotropy, based on *sudden* changes of internal energy, and concludes that the allotropy of iron is established. The magnetic property is a most suitable one to test this point,* yet Honda's curves † show no decisive discontinuity at A_3—the magnetization temperature curves have a definite slope (which varies in different experiments), and the ends are rounded off just as if the property changed rapidly yet continuously.

As mentioned in the conclusion of my Paper, the advantage of the definition I have adopted is that we do not require to determine what is happening *at* a certain temperature, but upon the sum total of what has happened *over an interval of temperature* including the point at which the transition takes place. Mr. Thompson refers to the transition at A_3 as a "de-crystallization" followed by a re-crystallization, and says that we cannot state exactly the quantity of heat evolved, due solely to allotropic change. We are, however, not concerned with the amorphous state at all in the thermal argument. All we have set out to discuss is the difference in structure between β iron and γ iron, and what happens at an intermediate point does not influence our argument. On the other hand, the existence of the amorphous state is, in my opinion, an indication of the continuity of the transition at A_3.

The statement on p. 137 that "These crystallographic results point merely

* *Science Reports*, Tokio, vol. iv., p. 170, 1915. † Ibid., p. 261.

to a different mode of packing of the iron molecules, which, beyond suffering slight distortion as a result, might be essentially unaltered. The magnetic work of Weiss has rendered it highly probable, however, that the differences extend beyond the mere molecular packing, each molecule having a definite different atomicity. Combining these two results, the question of the allotropy of iron "seems to have been placed beyond question," has been considered on p. 155 above.

Mr. Thompson says further (p. 138): "The final proof that this definition of allotropy is too narrow is obtained from the fact that, since the heat change per gram is but 3·2 gram-cal., the transition from rhombic to monoclinic sulphur is not an allotropic one." This is true provided we accept the transition in sulphur as allotropic. "Polymorphic" appears to be a more suitable term to describe the two forms of sulphur (Mitscherlich), for up to the present we have no proof that these two varieties are not merely two different physical aggregations of identical molecules.*

The effects of pressure and dissolved substances on the temperature of transition are very interesting. But purely physical change-points (e.g. fusion points) which are not accepted by many as allotropic behave in the same way, and so we cannot use these effects as a criterion of allotropic change.

Note added February 2, 1916.

After referring to Nernst's definition of allotropy as "a *sudden* change of internal energy," Mr. Thompson states (p. 136, bottom), "A total recrystallization with a different system, e.g. rhombic to tetragonal, together with alterations . . . do not, according to Dr. Oxley, denote allotropy, since the heat change accompanying them is small. Such a standpoint will result merely in a multiplication of terms, since some other name must be found for changes of this kind." Now, turning to Mr. McCance's remarks (p. 145), we find, "So in seeking for a definition let us not neglect the obvious evidence and . . . let an allotropic change be defined as a change in crystalline symmetry." In view of the slight alteration of crystalline form in iron at A_3, as compared with that at the transition-point of sulphur or tin, ought not the same argument to reject the term "allotropic" as inapplicable in the case of the A_3 transition of iron? According to Mr. Thompson's view, some other name must be found for this transition if the definition of Mr. McCance is adopted.

Most of the main points brought forward by the speakers at the meeting have now, I think, been considered. I think it may be said that the views expressed show a wide difference in the conception of the term "allotropy," even among metallurgists themselves. To some, difference of crystalline symmetry is the criterion, to others the discontinuous variation of some property is necessary, while some speak of the phenomenon vaguely as "certain energy and volume changes." None of these is so precise as the conception of "allotropy" as displayed by the oxygen to ozone transformation, which transformation involves a rebuilding of the atomic structure of the molecule. Moreover, this transformation is accepted by all as allotropic, and, accordingly, this type was taken by me purely for the sake of definiteness.

In conclusion, it may be said that the discussion has disclosed the fact that there exists a considerable vagueness in the modern conception of the term "allotropy," and some "sifting" is necessary if the term is to retain a definite scientific meaning such as modern research in metallography demands.

* See p. 153 above, and Tutton, *Crystals*, pp. 135–9.

THE TRANSFERENCE OF ELECTRICITY BY COLLOIDAL PARTICLES.

By FRANK POWIS, M.Sc.

(*A Paper read before the Faraday Society on Tuesday, October* 19, 1915. Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

On applying an e.m.f. to electrodes immersed in a colloidal solution the particles usually travel towards either the anode or cathode, and therefore behave as if they carried an electric charge. The formula

$$e = \frac{6\pi\eta r u}{H}$$

where—

e = mean charge carried by the particles ;
η = viscosity of medium ;
r = mean radius of the particles ;
u = velocity of the particles ;
H = potential gradient ;

has been used * to calculate the mean charge carried by the particles in a colloidal solution.

Another method of calculating the value of e, however, appears possible. For if we know the number of particles present in unit volume and their velocity under unit potential gradient, we can calculate what amount they would contribute to the conductivity of the solution if they carried a charge equal to n times that on a univalent ion. Conversely, if we knew what part of the conductivity was due to the transference of electricity by the colloidal particles we could calculate the mean charge carried by them. The difficulty is, of course, in determining this. But in the case of colloidal solutions of the noble metals prepared by sparking, the amount of foreign electrolyte present is exceedingly small, none being intentionally added to the conductivity water used. We might therefore reasonably attribute any increase in conductivity that occurs on making such a solution to the transference of electricity by the colloidal particles, and from this calculate the mean charge carried by them.

The number of cases in which the necessary measurements for such a calculation have been made seems to be extremely small, the only one I have found being by Burton,† for a coarse silver sol. The conductivity of the water was $3{\cdot}0 \times 10^{-6}$ mho, and of the colloidal solution 19×10^{-6} mho, at 18°. The solution contained 3×10^{8} particles per c.c., their average radius being $1{\cdot}7 \times 10^{-5}$ cm. Under a potential gradient these moved with a velocity of $23{\cdot}6 \times 10^{-5}$ cm./sec. per volt/cm. towards the anode. In this case, using the same method as Zsigmondy, we get—

$$e = 6 \times 3{\cdot}14 \times 0{\cdot}0105 \times (1{\cdot}7 \times 10^{-5}) \times (23{\cdot}6 \times 10^{-5})/_{300}$$
$$= 2{,}385 \times 10^{-10} \text{ electrostatic units,}$$

* Ellis, *Zeitschr. physikal. Chem.*, 1911, **78**, 321 ; Zsigmondy, *Kolloidchemie*, p. 51, pub. by Spamer, Leipzig, 1912.

† *Phil. Mag.*, [6] **11**, 425, 1906.

or 795 times the charge on a univalent ion, taking the latter as 3×10^{-10} electrostatic units.

In a solution containing 3×10^8 particles per c.c., each moving with a velocity 23·6 cm./sec. per volt/cm. and having a charge $= n$ times that on a univalent ion, the conductivity would be

$$\frac{3 \times 10^8}{7 \times 10^{23}} \times \frac{23{\cdot}6 \times 10^{-5}}{1{\cdot}036 \times 10^{-5}} \times n = 9{\cdot}8 \times 10^{-15} n \text{ mho},$$

since a solution containing 7×10^{23} univalent ions (1 gram-ion), each moving with an absolute velocity of $1{\cdot}036 \times 10^{-5}$ cm./sec. per volt/cm., i.e. 1·00 on the scale usually employed for conductivity numbers,* has a conductivity of 1 mho.

Both the conductivities given by Burton are high, pointing to the presence of a relatively large amount of electrolyte. For the purpose of the present calculation it therefore appeared better to utilize some values given by Billitzer, who, according to Müller,† paid special attention to the contribution of the particles to the conductivity of the "solution." In one case, using water of conductivity $0{\cdot}81 \times 10^{-6}$ mho, he obtained a colloidal platinum solution with a conductivity of $1{\cdot}1 \times 10^{-6}$ mho, i.e. an increase of only $0{\cdot}3 \times 10^{-6}$, this being apparently the smallest increase ever found.

Assuming that this small increase is due entirely to the transference of electricity by the colloidal particles, and using it in conjunction with Burton's values for the number of particles and their velocity (these being fairly normal values), we should have $9{\cdot}8 \times 10^{-15} n = 0{\cdot}3 \times 10^{-6}$, and therefore $n = 3 \times 10^7$.

Since, however, the colloidal solution as a whole is uncharged, if the particles carry a negative charge there must be some positive ions present to balance this, and these will help to increase the conductivity. Consequently the value of n will be less than that just calculated. As we are dealing with an aqueous solution, whatever the nature and origin of the positive ion, its mobility will probably not exceed that of the hydrogen ion. Assuming, then, that for every particle present, each of which has a negative charge n, there are present n positive monovalent ions, each moving with a velocity equal to that of the hydrogen ion, we get for the conductivity due to the particles and these positive ions (taking the mobility of $H^{\cdot}$ as 318)—

$$\frac{3 \times 10^8}{7 \times 10^{23}} \times \left(\frac{23{\cdot}6 \times 10^{-5} n}{1{\cdot}036 \times 10^{-5}} + 318n \right) \text{mho},$$

and if we put this $= 0{\cdot}3 \times 10^{-6}$ mho, we get $n = 2 \times 10^6$. This value, though less than the preceding one, is much higher than that calculated above, using the modified Stokes's formula. If the positive ion has a mobility less than that of the hydrogen ion, the value of n becomes larger still.

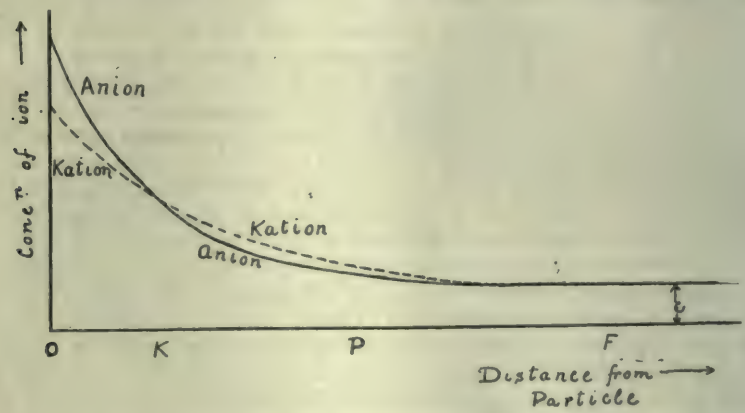
Exactly the same result is obtained if we adopt the more usual view that ions are adsorbed by the particles, so that at the surface of each one there is a layer of anions which move with it under the influence of an applied e.m.f., and outside this a layer of kations which move in the opposite direction with their usual velocity. If each particle adsorbs n anions and n kations (assuming both monovalent), it is easily seen that we obtain a value for n equal to the preceding one if the kation is $H^{\cdot}$, and greater if it is some other ion.

Various reasons might be suggested to account for the divergence in the numbers obtained by the two methods. For instance, as Zsigmondy points out in a footnote, if the particles adsorb ions their radius will be increased,

* Nernst, *Theoretical Chemistry*, third edition, p. 372.
† *Chemie der Kolloide*, p. 45.

and therefore the value of e calculated by his method would increase in the same ratio. Also part of even the small increase in conductivity of $0{\cdot}3 \times 10^{-6}$ mho might be due to the formation of some electrolyte during sparking, though with platinum and very pure water this appears unlikely. It may also appear somewhat arbitrary to combine Billitzer's conductivity values with Burton's data for the number and the mobility of the particles, but if Burton's conductivity values are used the divergence becomes greater still.

The author believes, however, that a colloidal particle adsorbs anions and kations, not so that they form two distinct layers round it, as seems to be generally supposed, but in such a way that the concentration of each gradually decreases with increasing distance from the particle until it finally becomes equal to that in the bulk of the surrounding medium. The accompanying diagram might make my conception clearer, this being for a negative colloid where the adsorbed anions and kations are of equal valency. For a positive colloid anions and kations would be interchanged. It will be seen that the concentration of each kind of ion approaches asymptotically that in



the bulk of the surrounding medium (c), and becomes equal to this at the same distance (OF) from the particle. In the layers between O and K the anions are in excess, whereas between K and F the kations are in excess. The total number of kations present up to F, however, must equal that of the anions, and therefore up to any distance OP smaller than OF the anions will be in excess.

The movement of the particle under the influence of an electric field is easily explained on this view. At a distance almost equal to OF the particle will exert only a small attractive force on the ions, and so their velocity will be almost normal. On the other hand, in the layers very near the particle, the force of adsorption will bind the ions so strongly to the particle that they cannot move without taking it with them. With a negative colloid these layers contain an excess of anions, and therefore the total force towards the anode will exceed that towards the cathode: the resultant force will therefore be towards the anode, and consequently the particle behaves as if it carried a negative charge. The observed velocity of the particle gives the velocity, in sign as well as magnitude, of both the anions and kations in the layers immediately adjacent to it; between this and F the velocity of the ion will gradually vary with its distance from the particle until it becomes normal at F, since here the adsorptive force is zero.

If the two ions are not of equal valency, then one divalent ion will be equal to two monovalent ones, etc. Other things being equal, it seems probable that a larger *proportion* of the divalent ions adsorbed, i.e. present up to the distance F, would be present in the layers near the particle, than of the monovalent ions. This might explain the predominating influence which ions of higher valency usually exert. With two electrolytes, both kinds of anion and kation will be adsorbed, and it will depend on their character and concentration whether the anions exceed the kations in the layers nearest the particle (giving a negative colloid), or vice versa (giving a positive colloid).* The effect on the velocity of the particles of adding an electrolyte to a colloidal solution is easily explained in this way, since it will influence the extent to which the anions or kations are in excess in the layers nearer the particle.

Exactly similar considerations will of course apply to larger suspended particles. With regard to electro-endosmosis, the walls are fixed, and the ions in the layers very near them will also be fixed, owing to the adsorptive force ; consequently the adjacent water is repelled in the direction opposite to that in which the wall tends to move.

On this view we should not be able to calculate the charge on the particles either from the modified Stokes's formula or from the increase in conductivity—in fact, there is no charge in the usual sense of the term—but we might calculate the minimum concentration of ions which would be required to give this extra conductivity. If the adsorbed ions be OH' and $H^{\cdot}$, then other water molecules would ionize in the bulk of the medium in order to keep the product $C_{H^{\cdot}} . C_{OH'}$ constant, and therefore the total conductivity should exceed that of the water. But if the adsorbed ions were from impurities present, the conductivity of the colloidal solution might be less than that of the water used ; the fact of this never having been observed is perhaps due to the greater tendency for reaction during sparking when appreciable amounts of electrolyte are present. Assuming all the anions to be OH' and all the kations $H^{\cdot}$, and taking the mobilities of these as 174 and 318 respectively, the extra concentration of each to give a conductivity increase of $0{\cdot}3 \times 10^{-6}$ mho would be 6×10^{-7} gram-ions per litre. This would be the value if the additional ions were distributed equally throughout the whole of the medium, and were free to move with their usual velocity, whereas above we assumed them to be concentrated near the particles, and most of them to be less mobile than usual. Both these would require $C_{H^{\cdot}}$ and $C_{OH'}$ near the particles to have a much higher value than that given above, and therefore the product $C_{H^{\cdot}} . S_{OH'}$ to have a value greatly exceeding its normal one. This does not appear improbable, however, since substances adsorbed by fine particles are usually regarded as being in a highly concentrated form.

Addendum.

When this paper was ready for despatch, an abstract appeared in the *Journal of the Chemical Society* issued on July 1 of a paper by H. Nordenson in the *Kolloid Zeitsch.*, 1915, **16**, 65, which in some parts would appear to be similar to the above. Since, however, this journal is not generally available here at the present time, I have not been able to see the original and find out how far they coincide. The best course therefore appeared to be the submission of the above as it stood.

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* See *Journ. Chem. Soc.*, 1915, **107**, 818, and *Zeitschr. für physikal. Chem.*, 1914, **89**, 91.

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION.

Preliminary Note.

By WILLIAM CLAYTON.

(*A Paper read before the Faraday Society on Tuesday, October* 19, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

Whilst the *photochemical* decomposition of hydrogen peroxide has been investigated in some detail (most recently by Matthews and Curtis),* the *thermal* decomposition, on the other hand, has received relatively little attention. The ultimate object of the present work was to investigate the latter with the object of bringing it into relation, if possible, with the photochemical. This was considered to be of special importance from the standpoint of homogeneous catalysis in view of the conclusions reached by Matthews and Curtis,† the chief of which are :—

(1) The photolysis of hydrogen peroxide proceeds smoothly at constant temperature and illumination, following the course of a monomolecular reaction. The reaction ceases abruptly upon extinguishing the light.

(2) The temperature coefficient of the light reaction is 1·5 approx.

(3) The same catalysts do not affect the thermal and photochemical decomposition of hydrogen peroxide in the same way. Thus the authors state that caustic soda inhibits the photochemical whilst it accelerates the thermal decomposition.

Practically all the research on the thermal decomposition of hydrogen peroxide deals not with the pure water case, but with aqueous solutions containing alkalis, salts, catalytic metals, and conserving agents. The only attempt at a complete investigation of the thermal decomposition in pure water is that of Lemoine,‡ who sought to determine how the velocity of the reaction varied with temperature and concentration. Lemoine concluded that the reaction was truly monomolecular, and that the temperature coefficient was from 2 to 3. Great discrepancies, however, are exhibited in the lists of constants for any given initial concentration of solution at a given temperature.

The following are a few of Lemoine's results :—

H_2O_2 per Cent.	Temperature. °C.	Values of K, the Monomolecular Constant.					
98	100	1·46	3·38	3·80	—	—	—
57	,,	3·56	2·83	7·96	2·85	1·71	—
56·5	,,	4·39	1·95	6·03	6·42	6·11	1·60

Lemoine concluded that the state of the surface of the containing vessel is the most important factor. This conclusion is discussed later in the light of the results communicated in the present paper.

Although an initial period of induction (real or apparent) is not known

* *Journ. Phys. Chem.*, **18**, 166, 521 (1914). † Loc. cit.

‡ *Journ. Chim. phys.*, **12**, 1–57 (1914).

in the photochemical decomposition,* Lemoine observed a period of induction, "une certaine inertie au début," for the thermal reaction in concentrated solutions, especially at fairly low temperatures, the evolution of oxygen being inhibited for a time. He gives the following data :—

Temperature. ° C.	H_2O_2 per Cent.	Period of Inertia. Hrs. min.
35·5	84·6	6 6
36·0	86·0	2 0
36·0	72·5	1 5
36·0	66·0	1 37
36·0	64·0	5 8

Similar induction periods have been observed in certain instances in the present work, though the solutions were dilute and the temperature relatively high. Thus a solution (1·5 per cent. H_2O_2) at 60°C. showed no change in strength for five hours. A similar solution remained unchanged for nearly four hours. In another case in which the 1·5 per cent. H_2O_2 solution (at 50° C.) contained NaOH (0·003 N) an induction period of at least eight hours was observed. Whether such effects are really characteristic of the reaction itself, or depend upon accidental impurity or the state of the walls of the vessel, cannot at this stage be definitely stated.

Experimental Methods and Results.

The material employed was Merck's perhydrol, diluted to the required amount. The rate of decomposition was determined by pipetting out certain quantities of the solution and titrating with N. 10 $KMnO_4$ in H_2SO_4 solution. The decomposing solutions were placed in various flasks (Jena glass, wax-lined flasks, and quartz) suspended in electrically controlled thermostats at 50° C. and 60° C. respectively. The withdrawal of aliquot portions was carried out by means of a special pipette designed to avoid the difficulty of reading when rapid gas evolution occurred.†

The velocity constant of decomposition was calculated by the usual monomolecular expression—

$$K = \frac{1}{t} \log \frac{a}{a - x},$$

the values of K being obtained directly from the experimental numbers by employing logarithms to the base 10. The reaction is treated (in this preliminary investigation at any rate) as monomolecular because of the simple type of reaction involved, and also because of the fact that hydrogen peroxide in aqueous solutions is known to exist in an unpolymerized state.‡ In view, however, of the discrepancies observed in the values of the "constant," other "constants" were calculated, viz. that corresponding to a zeromolecular reaction $\frac{dx}{dt} = k$, and that corresponding to a bimolecular reaction. These values afforded no better agreement. Lemoine § also concluded that the bimolecular equation did not hold.

As an illustration of what may be regarded as a relatively concordant set of values, two experiments carried out at 50° C. in a quartz flask containing conductivity water may be cited.

* Matthews and Curtis, loc. cit.

† Cf. Walton and Judd, *Zeitschr. physik Chem.*, **83**, 315 (1913).

‡ Cf. Carrara, *Zeitschr. physik. Chem.*, **12**, 498 (1893); Orndoff and White, ibid. **12**, 431 (1893); Tammann, ibid. **12**, 63 (1893).

§ Loc. cit.

Initial concentration of H_2O_2 = 1·5 per cent.

Time (min).	$a - x$.	K (monomolecular).
0	42·4	—
95	41·5	0·000100
1,199	33·4	0·000086
2,657	25·0	86
2,976	23·5	86
4,114	18·3	88
4,230	18·0	88

The same experiment was repeated in a second quartz flask painted black on the outside to avoid photochemical effects.

t.	$a - x$.	K.
0	43·0	—
231	40·9	0·0000943
1,357	30·9	0·0001057
1,597	28·9	0·0001080
2,757	21·5	1092
3,040	20·05	1090
3,292	18·75	1095
4,182	14·90	1100
5,688	10·10	1106
6,012	9·30	1106
7,093	7·10	1102
9,958	3·40	1106
	Mean ...	0·0001093

Later results with alkaline solutions of hydrogen peroxide showed much greater variations, as also did measurements in conductivity water at 60° C. The research therefore resolved itself into a search for the possible cause or causes of these variations.

At the temperatures 50° to 60° C. the possible volatility of H_2O_2 has to be considered. It was tested for as follows : A flask containing the H_2O_2 solution was suspended in a thermostat at 50° C., and by means of a puff-ball the gases above the solution could be swept out of the flask and made to pass into a very dilute acid solution of $KMnO_4$. The gases were swept out at intervals for two days. Not the slightest trace of H_2O_2 could be detected. A repetition of this experiment at 60° C. confirmed the result, and it was therefore concluded that the discrepancies could not be due to this cause.*

Possible loss of water vapour was prevented by closing the flasks with long air-cooled glass tubes, serving as condensers. Later, in order to avoid the possibility of dust entering the solutions and so catalysing the reaction, wax-lined tin caps, loosely fitting, were provided for the various flasks.

An interesting question also arises as to whether stirring the solutions would influence the rate of decomposition. Lemoine† has concluded that no appreciable influence manifested itself if the solutions were agitated, if the pressure were altered, or if dust-free gases (O_2 and H_2) were bubbled through the solutions. Several stirring experiments were therefore carried out using a glass stirrer rotating moderately fast ; the conclusion reached being that stirring has no appreciable effect upon the rate, at least within the limits of the experimental measurements.

* As further evidence for the involatility of H_2O_2 at the temperatures mentioned, compare Nernst, *Zeitschr. Elektrochem.*, **11**, 710 (1905). † Loc. cit.

To return to the problem of the decomposition of H_2O_2 in alkaline solutions, it may be mentioned that the caustic soda employed had been precipitated by alcohol. It was used at various concentrations, but satisfactory results could not be obtained. A single illustration will serve to indicate the degree of variability observed.

1·5 *per Cent.* H_2O_2 *in* N. 10 *NaOH.*

(*Duplicate Experiments.*)

Experiment I.			Experiment II.		
t.	*x.*	K (monomolecular).	*t.*	*x.*	K.
24	12·45	0·011016	26	16·10	0·01142
35	15·40	0·010306	53	21·50	0·00887
46	16·85	0·009067	109	25·80	0·00629
64	18·90	0·007998	241	29·50	0·00429
157	19·73	0·004670	343	30·53	0·00390
201	21·00	0·004044	∞	[32·50]	
257	22·15	0·003503			
∞	[27·30]				

It will be observed that K falls as the reaction proceeds.

Similar variations in results were obtained in many other cases, e.g. using NaCl, mixtures of NaCl and NaOH, Na_2SO_4, and $NaNO_3$. A search of the literature showed that previous workers had met with similar difficulties, e.g. Tammann,* who investigated the effect of alkali upon the peroxide. Tammann attributes the variability to the presence of iron oxide in the alkali. This conclusion appears to be probable inasmuch as the stock solution employed for the present experiments deposited on long standing a light-brown precipitate of iron hydroxide. To test this point directly a solution of H_2O_2 (1·5 per cent.) in good conductivity water had a trace of colloidal iron hydroxide added to it, and the rate of decomposition at 50° C. was followed. The mean velocity constant was 0·00077, whilst that with conductivity water alone is of the order 0·00010. That is, the velocity constant in presence of the iron is seven times that in its absence.

The question of the influence of the *surface* of the containing vessel has already been referred to. Lemoine showed that a solution of H_2O_2 at 21° C., normally requiring 15 days for half-decomposition, required only 3 minutes when placed in a silvered tube. The writer has confirmed this result, viz. a reaction (1·5 per cent. H_2O_2 at 60° C.) normally requiring 23 hours for half-decomposition went to completion in less than half an hour when kept in a silver bottle. In this connection, Spring had already shown † that a solution of H_2O_2 would keep well in a vessel of clean smooth platinum, but the slightest scratch accelerated the reaction markedly. Further, it is generally accepted that quartz flasks are more advantageous than glass ones for conserving H_2O_2, and, following Brühl's observation that a waxed surface is very inert, wax-lined bottles are used commercially for storing the peroxide.

The results obtained by the writer, however, seem to show that at temperatures from 50° C. upwards the nature of the containing vessel ‡ is not so vital as the degree of "purity" of the water which is employed as the solvent. With very "pure" water, the results show that the rate of decomposition is approximately the same whether the flask be of glass, quartz, or wax.

* *Zeitschr. physik. Chem.*, **4**, 440 (1889). † *Bull. Acad. roy. Belg.*, [3], **30**, 32 (1895).

‡ Provided it is not metallic.

Rate of Decomposition of H_2O_2 in Water of Various Degrees of "Purity."

Previous workers do not appear to have laid particular stress upon the "purity" of the water. It was considered, in the light of the foregoing work on the influence of colloids, that perhaps even good conductivity water was in reality unsuitable. Accordingly, a series of experiments was carried out in four different flasks, viz. (1) Jena glass, (2) quartz flask (X), (3) quartz flask (Y), (4) wax-lined flask. A number of solutions containing 1·5 per cent. H_2O_2 were made up in the following "solvents":—

(*a*) Tap water.
(*b*) Ordinary distilled water (from block-tin condenser).
(*c*) Conductivity water (conductivity 1·1 gemmho).
(*d*) "Pure water I."
(*e*) "Pure water II."

"Pure water I." was prepared as follows: A silver-plated copper boiler (3 pints capacity) was filled with freshly distilled water, which was then redistilled, the steam passing through two quartz spirals, the first to serve as a spray trap, the second as a condenser. The water was collected directly in the reaction flask. (No glass was employed in the apparatus.)

"Pure water II." was prepared as described above, with the addition that the quartz arm connecting the two spirals was heated to redness so that the dry steam might deposit any suspended matter.

The results obtained with these various solvents are appended in Tables I to V.

TABLE I.

Tap Water as Solvent. 1·5 *per Cent.* H_2O_2 *at* 60° C.

$K = \frac{1}{t} \log \frac{a}{a-x}$. $t_{\frac{1}{2}}$ = *time of half decomposition.*

QUARTZ FLASK X.

	Experiment (*a*).		*Experiment* (*b*).
t (min.).	*x*.	K.	
21	1·15	0·00115	
128	6·65	128	
255	12·45	151	
292	13·85	158	
343	15·35	163	
474	18·45	188	
	[21·15]		
	$t_{\frac{1}{2}}$ = 3 hrs. 33 min.		$t_{\frac{1}{2}}$ = 4 hrs. 26 min.

TABLE II.

Distilled Water as Solvent. 1·5 *per Cent.* H_2O_2 *at* 60° C.

QUARTZ FLASK Y.

	Experiment (*a*).			*Experiment* (*b*).	
t.	*x*.	K.	*t*.	*x*.	K.
60	0·50	0·000166	81	1·15	0·000291
195	1·20	124	239	2·30	207
416	3·40	175	418	3·95	208
1,389	8·85	160	1,413	9·75	182
1,509	9·40	160	1,839	11·50	177
2,791	13·70	151		[21·75]	
3,184	14·80	152			
4,269	16·95	149			
	[22·00]				
	$t_{\frac{1}{2}}$ = 32 hrs. 34 min.			$t_{\frac{1}{2}}$ = 28 hrs.	

TABLE III.

Conductivity Water as Solvent. 1·5 *per Cent.* H_2O_2 *at* 60° C

Repetition of same experiment in same flasks under identical conditions. Conductivity water employed ($1·1 \times 10^{-6}$ mho.)

(1) JENA GLASS.

t.	*x.*	K.
99	0·55	·000122
214	1·50	157
420	3·00	167
1,394	9·30	193
1,523	9·95	194
1,752	11·56	212
2,844	18·10	352
3,000	18·40	357
	$t_{\frac{1}{2}}$ = 25 hrs. 12 min.	
47	0·65	·000293
178	2·20	266
318	3·70	267
1,316	10·60	235
1,492	11·20	225
1,683	12·53	238
	$t_{\frac{1}{2}}$ = 20 hrs. 12 min.	
48	0·35	·000153
129	0·55	·00009
1,106	7·80	·000186
1,346	8·85	180
2,569	13·65	182
2,923	14·60	182
4,003	16·95	186
	$t_{\frac{1}{2}}$ = 27 hrs.	

(2) QUARTZ X.

t.	*x.*	K.
99	1·20	·000260
216	2·45	251
410	4·30	245
1,399	11·40	246
1,528	12·05	246
1,730	13·00	246
2,848	16·70	247
2,985	17·00	246
	$t_{\frac{1}{2}}$ = 20 hrs. 12 min.	
108	1·15	·000225
261	3·55	306
1,251	11·40	269
1,438	12·50	271
1,616	13·27	266
	$t_{\frac{1}{2}}$ = 18 hrs. 36 min.	
48	0·65	·000283
117	2·40	254
1,105	8·45	201
1,354	10·30	214
1,482	11·30	224
2,574	16·50	256
2,924	17·40	258
4,008	20·15	337
	$t_{\frac{1}{2}}$ = 23 hrs.	

(3) QUARTZ Y.

t.	*x.*	K.
45	0·30	·000138
1,098	5·35	116
1,355	7·20	130
1,488	7·85	136
2,580	11·60	135
2,925	12·20	129
4,004	15·05	136
	$t_{\frac{1}{2}}$ = 43 hrs.	
92	0·75	·000175
210	2·40	256
406	4·40	257
1,390	9·80	201
1,722	10·90	189
2,839	14·30	181
2,975	14·50	177
	$t_{\frac{1}{2}}$ = 28 hrs.	

(4) WAX-LINED FLASK.

t.	*x.*	K.
58	0·75	·000270
276	8·35	272
383	4·55	275
1,433	10·55	210
1,758	11·70	200
2,852	14·60	180
	$t_{\frac{1}{2}}$ = 23 hrs. 50 min.	

TABLE IV.

"Pure Water I." as Solvent. 1·5 *per Cent.* H_2O_2 *at* 60° C.

JENA GLASS.

t.	*x.*	K.
49	0·35	0·000144
161	0·50	0·000063
346	0·80	47
1,377	1·95	29
2,896	4·00	30
4,248	5·40	29
5,777	6·10	25
7,068	7·82	27
8,514	9·34	28
9,963	10·96	30
	[21·70]	

$t_{\frac{1}{2}} = 165$ hrs.

QUARTZ X.

Experiment (a).

t.	*x.*	K.
121	0·45	0·000077
296	1·35	0·000094
1,048	4·60	0·000102
1,368	5·90	0·000105
2,480	9·85	111
2,958	11·10	110
3,981	13·30	109
5,475	16·05	115
	[20·95]	

$t_{\frac{1}{2}} = 45$ hrs.

Experiment (b).

t.	*x.*	K.
137	0·85	0·000127
321	1·55	0·000097
1,301	2·47	40
2,710	6·16	53
4,152	9·24	58
5,602	11·59	59
	[21·55]	

$t_{\frac{1}{2}} = 81$ hrs.

QUARTZ Y.

Experiment (a).

t.	*x.*	K.
117	0·05	0·000009
254	0·25	0·000021
1,365	2·55	43
1,844	3·30	42
2,867	5·40	46
4,362	8·05	50
5,870	10·20	51
7,198	11·75	51
	[20·35]	

$t_{\frac{1}{2}} = 98$ hrs.

Experiment (b).

t.	*x.*	K.
144	0·80	0·000115
297	1·30	0·000092
1,313	3·07	51
2,714	6·98	63
4,154	10·17	67
5,600	12·85	71
	[21·30]	

$t_{\frac{1}{2}} = 70$ hrs.

WAX-LINED FLASK.

Experiment (a).

t.	*x.*	K.
53	0·15	0·000058
293	0·65	45
1,295	3·85	65
1,775	5·35	69
2,796	7·55	66
3,229	8·35	65
4,275	10·30	65
5,792	12·20	62
7,135	13·55	59
	[21·65]	

$t_{\frac{1}{2}} = 71$ hrs.

TABLE V.

"Pure Water II." as Solvent. 1·5 per Cent. H_2O_2 at 60° C.

JENA GLASS FLASK.			WAX-LINED FLASK.		
t.	*x.*	K.	*t.*	*x.*	K.
165	0·30	0·0000375	234	0·10	0·000009
1,198	2·10	381	1,334	1·45	0·000026
2,619	3·80	331	2,637	2·70	25
4,449	5·40	290	4,124	4·10	26
6,497	8·20	330	5,559	5·00	24
7,992	9·70	336	6,946	5·85	23
9,723	11·70	318	8,485	6·90	23
	[21·00]				
	$t_{\frac{1}{2}} = 143$ hrs.				

QUARTZ X.			QUARTZ Y.		
t.	*x.*	K.	*t.*	*x.*	K.
351	0·75	0·0000490	220	0·45	0·000048
1,440	1·70	282	1,337	2·15	40
2,730	2·55	238	2,608	4·45	45
4,202	3·05	180	4,000	7·55	56
5,660	4·30	196	5,440	10·20	63
7,056	5·05	190	6,856	12·55	74
8,589	6·05	193	7,374	14·50	89

It will be observed that with this solvent the lowest values so far have been obtained, viz. with quartz flask X and the wax-lined flask, the order of magnitude of K being 0·00002. This is approximately one-tenth of the value obtained with conductivity water, and further, the rate in conductivity water is scarcely distinguishable from that in ordinary distilled water. It may be inferred, therefore, that the hydrogen and hydroxyl ions of the solvent do not exercise an appreciable influence, but that the freedom of the solvent from colloidal organic matter is the factor of greatest importance.

At this stage the work had to be interrupted. Although the results are preliminary only, it is believed that the following conclusions are justifiable.

SUMMARY.

1. The rate of thermal decomposition of aqueous solutions of hydrogen peroxide is extremely sensitive towards extraneous organic matter in the colloidal state. Mechanical factors, such as volatility and the presence or absence of stirring, do not exercise an appreciable influence.

2. The chief factor in the decomposition has been shown to be the degree of purity of the water. Thus in tap water the rate of decomposition is fully fifty times that in the purest specimen of water we have yet prepared.

3. In the light of these results, previous work upon the thermal decomposition of H_2O_2, especially the comprehensive research of Lemoine, must be considered as of doubtful value, as no special precautions appear to have been taken in regard to the solvent.

4. In view of the marked effect produced by the solvent it remains an open question as to whether the surface of the vessel exerts an appreciable effect or not; it is possible that effects previously attributed to the surface may have been due to slight variations in the organic-matter content of the solvent.

In conclusion, the author wishes to express his thanks to Professor W. C. McC. Lewis for suggesting and supervising the research.

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THE ELECTROLYSIS OF NITRIC, SULPHURIC, AND ORTHOPHOSPHORIC ACIDS, USING A GOLD ANODE.

By F. H. JEFFERY, M.A.

(*A Paper read before the Faraday Society on Tuesday, October* 19, 1915, Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

Some of the effects of using a gold anode in certain cases of electrolysis are described in the course of a paper by Lenher ; * for solutions of sulphuric acid and of potassium sulphate a more detailed account is given by Mixter. † In the following investigation further details are given of the reactions taking place with a gold anode. The cell used was formed of a Jena beaker of 800 c.c. capacity, inside which was a porous pot. The volume of the anolyte was about 550 c.c. The gold anode hung from a platinum wire in the beaker, the platinum being above the surface of the electrolyte. The platinum cathode was placed inside the porous pot. A glass stirrer turned by means of a motor revolved in the beaker close to the anode. The beaker and its contents were placed in a large vessel of cold water.

In all cases the solid gold compounds formed were quite homogeneous in appearance, and the analyses of samples obtained under the same conditions were consistent with this. The weight of gold entering into combination per faraday was small, being not greater than 2·5 grams in any of the following experiments.

Nitric Acid Electrolyte.

(i.) The concentration of acid used was that corresponding to 100 c.c. HNO_3 of density 1·42, diluted with 100 c.c. water. The temperature 12° C. to 16° C.

At first experiments were made without a porous pot around the cathode. A current of 4 amperes was used.

On closing the circuit much hydrogen was evolved at the cathode, and the difference of potentials at cathode and anode was 4·4 volts. After about one minute the voltage fell to 3·7 volts and hardly any gas was evolved at the cathode.

The current and voltage remained constant after the initial fall of voltage during several hours.

The electrolyte became of a pale yellowish-green colour, the cathode was covered with a brown solid, and the same brown solid was distributed throughout the electrolyte.

This solid was analysed. On heating it gave Au and H_2O only. It was dried for 3 hours over conc. H_2SO_4 in a vacuum desiccator, and gave 99·9 per cent. Au (0·3921 grams taken).

Au was precipitated from the green electrolyte by SO_2 and by HNO_2.

It appears, therefore, that gold is dissolved from the anode, forming a green compound, which is reduced to metallic gold by the hydrogen dissolved in the platinum cathode.

* *J. Amer. Chem. Soc.* 26, 550, 1904. † Ibid. 33, 688, 1911.

A series of experiments were made using a porous pot around the cathode. The acid used for the catholyte was of the same concentration as that used for anolyte. Various currents and current densities were employed.

The anode decreased in weight. During the solution of the gold no deposit was formed on it, neither was there finely divided gold distributed through the anolyte.

The cathode remained bright and entirely free from any deposit of gold. The acid in the pot was reduced to nitrous acid, nitric peroxide being evolved; also no gold was found on the inner surface of the pot.

The anode acid became a deep olive-green colour owing to the gold compound formed. As the electrolysis proceeded, the colour changed to a bright sherry hue, and finally to a deep yellow-brown. Gold was at once precipitated from the anolyte by HNO_2 and by SO_2.

It appears, therefore, that the gold goes into solution as complex anions. The colour changes may be due to changes in the relative proportions of the complex anions and the undissociated compounds to which they correspond, since dilution of the brown-yellow liquid with nitric acid of the same concentration as used originally for the anolyte reproduces the olive-green coloration.

The anolyte, whether at the green stage or later, when kept in a closed flask, deposited a fine black powder on the bottom of the flask. This was found to be pure gold.

Bright yellow metallic scales were formed on the surface of the liquid: these were also gold.

A weighed strip of gold was left in the anolyte for about 16 to 17 hours and then reweighed. No gold was dissolved. (Temperature about 15° C.) Some of the yellow-brown anolyte was kept at −16° C. for about 5 hours. No crystals were obtained. Hardly any of the fine black gold described above was formed.

Some of the same brown-yellow anolyte was placed in a vacuum desiccator over conc. H_2SO_4 with a vessel containing sticks of NaOH close to it. The HNO_3 distilled and metallic gold separated from the solution, and finally small lemon-yellow crystals were formed. These had the appearance of auri-nitric acid, $HAu(NO_3)_4{\cdot}3H_2O$.

These were analysed by adding to a known weight of the crystals a known volume of water. Nitric acid was formed in solution, and the orange-yellow insoluble solid formed at the same time was ignited and the gold obtained weighed. The percentage of gold in the crystals was found to be (*a*) 39·52, (*b*) 39·22, giving a mean 39·37.

The nitric acid was titrated with $KHCO_3$ solution, and the value of NO_3/Au was found to be (*a*) 3·95, (*b*) 4·08, giving a mean 4·01.

A small quantity of the orange-yellow solid was analysed for the gold to oxygen ratio by heating it and collecting the oxygen. This was found to be 8·26. The crystals were very hygroscopic, and appeared to be partially hydrolysed in contact with air containing water vapour.

For auri-nitric acid crystals the calculated percentage of gold is 39·42, the value of NO_3/Au is 4·00, and for hydrated Au_2O_3 the gold to oxygen ratio is 8·22.

It appears, therefore, that the crystals are auri-nitric acid.

Some of the yellow-brown anolyte was added to a large volume of cold water (temp. about 12° C.). An orange-yellow precipitate was obtained. This was washed and left under water for three weeks, the water being changed frequently. Finally the washings gave no acid reaction with litmus and no precipitate with nitron (diphenyl-endo-anilo-dihydro-triazole).

The powder was dried for 90 hours over conc. H_2SO_4 in a vacuum desiccator.

When heated, oxygen and gold were formed and water evolved, which was acid to litmus and contained a small quantity of nitric acid.

The proportion by weight of gold to oxygen = 8·34; for hydrated Au_2O_3 this proportion = 8·22.

The powder was completely soluble in cold dilute HCl.

The anolyte was electrolysed, using a platinum anode and a platinum cathode surrounded by a porous pot containing nitric acid diluted with its own volume of water. There was no deposition of gold on either electrode; the gold compounds in the anolyte did not appear to be affected by the passage of the current.

The quantity of gold dissolved per faraday of electricity was 0·0104 gram-atoms (Au = 197·2) for current of 1 ampere and anode area 2 × 4·61 cm.², the number given being the mean of ten determinations made when the anolyte was in the yellow-brown stage.

When the current was changed to 0·5 amperes, the anode area remaining the same, the mean of five determinations gave 0·0113 gram-atoms per faraday. (The quantity of electricity was measured by placing a water voltameter in circuit and collecting the hydrogen evolved in an Ostwald gas burette.)

It appears possible that the gold is dissolved partly in the trivalent state and partly in the monovalent state. The anion corresponding to the former appears to be derived from $HAu(NO_3)_4$, and to the latter possibly from $HAu(NO_3)_2$; the auri-nitric acid has been isolated, but the corresponding aurous compound is hypothetical.

When the anolyte is added to water hydrolysis takes place, and possibly a mixture of hydrated auric oxide and of Au_2O is formed, which would account for the high gold to oxygen ratio. This ratio corresponds to $Au_2O/Au_2O_3 = 0·02$. The difficulty of washing the product of hydrolysis free from HNO_2 may be due to the formation of a basic auric nitrate which is slowly decomposed in water.

The formation of the fine black gold when the anolyte is kept may be due to the gradual transformation of the aurous compound to the auric compound and gold. At — 16° C. such a reaction would proceed more slowly.

(ii.) An electrolyte was used of concentration corresponding to 100 c.c. HNO_3, density 1·42, diluted with 200 c.c. water. The anolyte became first olive-green and then yellow. At this stage a red-brown powder separated and was formed in increasing quantity as the electrolysis proceeded. There was no deposit adhering to the anode and no trace of gold on the cathode.

With a current of 1 ampere and anode area 2 × 7·10 cm.², 0·0118 gram-atoms of gold went into combination per faraday. When the powder had settled the yellow anolyte was poured off.

The brown powder was washed with water until the washings gave no acid reaction with litmus, nor any precipitate with nitron.

When heated alone gold and oxygen were formed, and also water, which was only very faintly acid to litmus.

The gold to oxygen ratio was determined by heating the solid and collecting the oxygen. This was found to be (*a*) 8·61, (*b*) 8·66, giving a mean 8·63—for Au_2O_3 the value is 8·22. The powder was completely soluble in cold dilute HCl.

Some of the same powder was left under KOH solution at room temperature. The greater portion dissolved. The yellow solution formed was poured off and fresh KOH solution added, the process being repeated during five weeks until the solution poured off ceased to contain any gold compound.

A small residue of violet-black powder remained.

This was washed with water and then dilute HCl was added to it. $HAuCl_4$ was formed and also a residue of gold.

It appears, therefore, that the brown powder is a mixture of hydrated Au_2O_3, which is dissolved by the KOH, and of Au_2O. The ratio of gold to oxygen corresponds to $Au_2O/Au_2O_3 = 0{\cdot}07$.

The yellow anolyte was poured into a large volume of water at about 14° C., and the product of hydrolysis washed and examined for the gold to oxygen ratio. This was found to be 9·26—considerably higher than that obtained for the brown powder described above.

The water evolved on heating was faintly acid to litmus.

These results seem also consistent with the hypothesis that a mixture of aurous and auric compounds is formed during the electrolysis.

(iii.) A nitric acid of smaller concentration was then used—100 c.c. acid to 400 c.c. water. The current was 1 ampere and the anode area was 9·80 × 2 cm.². Temperature 14° C. The fraction of the gold entering into combination which formed soluble compounds was small, the anolyte becoming a very pale green. A brown magenta solid was formed at the anode, adhering to it to a small extent.

This was washed and dried as previously described. When the solid was heated, gold, oxygen, and water were formed; the water was very faintly acid to litmus.

The mean value of the gold to oxygen ratio was 8·48—(*a*) 8·46, (*b*) 8·51.

The solid was completely soluble in cold dilute HCl. The number of gram-atoms of gold going into combination per faraday was 0·0114. A portion was placed in cold KOH solution. The greater part dissolved, and when finally the KOH solution left on the solid dissolved no more gold compound, there was a blackish residue, which as in the previous case was found to be Au_2O.

It appears, therefore, that the brown solid is a mixture of hydrated Au_2O_3, which is dissolved by the KOH, and of Au_2O. The ratio of gold to oxygen corresponds to $Au_2O/Au_2O_3 = 0{\cdot}05$.

The brown solid was soluble in cold nitric acid of concentration used for (i.), giving a greenish-yellow solution. This solution gradually deposited finely divided gold when kept in a closed flask. Its appearance and reactions were similar to those of the yellow-green anolyte obtained from the nitric acid of concentration used in (i.). It was placed in a vacuum desiccator over conc. H_2SO_4 with a dish containing sticks of NaOH close to it. When it had ceased to deposit gold, the clear solution was decanted and the nitric acid was allowed to distil until yellow crystals were obtained. These were analysed in the same way as described in (i.). With water they reacted, giving hydrated auric oxide and nitric acid. The percentage of gold in the crystals was found to be 39·21 and the ratio NO_3/Au to be 4·03. For auri-nitric acid $HAu(NO_3)_4{\cdot}3H_2O$ the corresponding numbers are 39·42 and 4·00. The crystals are therefore auri-nitric acid.

This result affords further evidence that the gold compounds in solution in the anolyte (i.) are derived from aurous and from auric gold. The proportions of the two compounds are, however, not the same in the anolyte (i.) as they are in the solution just described.

(iv.) A still more dilute nitric acid was used as anolyte, formed from 1 c.c. HNO_3 Δ 1·42 and 10 c.c. water.

Acid of the same concentration was used for catholyte.

The current used was 0·5 ampere and the anode area 2 × 12·9 cm.².

Care was taken to stop the electrolysis before all the catholyte was

reduced to $NH_4 \cdot NO_3$, and also before more $NH_4 \cdot NO_3$ had accumulated in the anolyte than would give a yellow coloration when 5 c.c. of Nessler solution was added to 10 c.c. of the anolyte neutralized with KOH and made up to 50 c.c. with water. (Undissociated $NH_4 \cdot NO_3$ slowly diffused through the pot into the anolyte.) With these precautions the brown solid formed at the anode was not explosive when heated.

No gold was deposited on the cathode, nor was there any trace of gold compound in the catholyte.

The anolyte contained sufficient soluble gold compound to give a purple coloration when SO_2 was passed into it. The brown solid was washed free from HNO_3, as in previous experiments, and dried *in vacuo* over conc. H_2SO_4. On heating it, gold, oxygen, and water were formed.

No NO_2 was evolved, but the water evolved was acid to litmus. The solid was analysed by heating it and collecting oxygen.

Analyses of two preparations gave the gold to oxygen ratio (*a*) 8·21, (*b*) 8·20.

It appears, therefore, that under these conditions hydrated auric oxide is formed, and that such of the gold as forms a soluble compound goes into solution as complex anions only. These probably correspond to $HAu(NO_3)_4$, as this compound is formed from Au_2O_3 and nitric acid. The acidity of the water evolved on heating the oxide is probably due to a small trace of a basic nitrate not hydrolysed during the process of washing.

Another experiment was made with an anolyte of this concentration, using the same anode area but a current of 1 ampere. The results were exactly similar to those described for a current of 0·5 ampere. Analysis of the anode solid gave (*a*) 8·25, (*b*) 8·24 for the gold to oxygen ratio.

This appears to be a fairly good method of preparing hydrated auric oxide, the only impurity present being a trace of combined nitric acid; it was found that by stirring the brown solid under water for some weeks and frequently changing the water the nitric acid present could be reduced to so small a quantity that the water evolved on heating the dry solid was only faintly acid to litmus.

The disadvantage of the method is that the hydrated auric oxide is formed slowly; under the conditions used only from 0·04 to 0·05 gram of gold go into combination per ampere hour.

(v.) An acid of concentration corresponding to 1 c.c. HNO_3 Δ 1·42 to 20 c.c. of water was used as anolyte. The catholyte acid was of twice this concentration.

The same precautions as to the accumulation of $NH_4 \cdot NO_3$ in the anolyte were taken as in (iv.). The current was 1 ampere, and the anode area the same as for the preceding experiment. The results were exactly similar to those described in (iv.).

Analysis of the anode solid gave (*a*) 8·21, (*b*) 8·20 for the gold to oxygen ratio.

In this case also hydrated auric oxide is therefore formed.

It is noteworthy that with acids of the concentrations used for (iv.) and (v.) no aurous compound is formed. Apparently the percentage of aurous compound in the solid formed at the anode decreases as the dilution of the nitric acid used for anolyte is increased, and finally a stage is reached beyond which practically pure hydrated auric oxide is produced.

If precautions are not taken to prevent accumulation of ammonium nitrate in the anolyte when dilute acids are used, a compound is formed at the anode which is violently explosive when heated. This compound is readily produced with an acid of concentration 1 c.c. HNO_3 Δ 1·42 to 20 c.c. water; it is

found intermixed with the hydrated auric oxide at the anode. At the stage at which this compound is formed a small quantity of black powder collects at the edges of the platinum cathode. This powder is gold. Hence under these conditions some gold cations are formed. Whether these are due to the decomposition of some complex ion has not yet been investigated, but it seems probable that a complex cation derived from gold and ammonium is formed.

Sulphuric Acid Electrolyte.

(i.) The concentration of acid used was that corresponding to 100 c.c. H_2SO_4 of density 1·84, diluted with 100 c.c. water. The temperature 18° C. to 20° C.

The platinum cathode was surrounded by a porous pot. The same acid was used for catholyte as for anolyte. The current was 2·5 amperes and the anode area $2 \times 11{\cdot}74$ cm.^{2} During the electrolysis the anode decreased in weight; no deposit was formed on the anode. The anolyte became of a deep olive-green colour, and gave an immediate precipitate of gold on the addition of SO_2. A fine yellow powder was distributed throughout the anolyte; this was found to be pure gold. At this stage there was no trace of gold on the cathode.

Some of the green liquid was electrolysed, using a platinum anode and a platinum cathode surrounded by a porous pot containing dilute sulphuric acid. The gold was completely removed from the compounds in the anolyte and deposited on the anode; there was no trace of gold on the cathode.

It appears, therefore, that the gold from the gold anode goes into solution as complex anions.

The electrolysis with the gold anode was continued; the anolyte became of a bright yellow colour, and finally of a deep yellow-brown. There was increasing formation of the finely divided yellow gold throughout the anolyte.

At this stage there was a small deposit of gold on the cathode. When this yellow-brown anolyte was electrolysed with platinum electrodes, as was done for the green anolyte, there was no decomposition of the gold compounds present.

The anode potential of the gold anode was taken during the electrolysis, using as normal electrode $Hg \mid Hg_2SO_4$, 2N. $H_2SO_4 \mid$, as described by Sand. For a steady current of 2·5 amperes this remained constant throughout the changes from the green to the dark yellow-brown stage and while the gold was deposited on the cathode.

It appears, therefore, that the gold goes into solution for the most part as complex anions, but that at the yellow-brown stage an appreciable quantity of cations are formed. None the less, the concentration of the cations in the neighbourhood of the anode must remain constant and very small. It is possible that the gold ions reaching the cathode may arise from the dissociation of the complex anions. A probable alternative is that some of the undissociated compound corresponding to the complex anions has diffused into the catholyte and has been reduced by the hydrogen at the cathode. The colour changes in the anolyte may be due to changes in the relative proportions of the complex anions and the undissociated compounds to which they correspond; the green colour is restored when the yellow-brown anolyte is diluted with sulphuric acid of the same concentration as originally taken for the anolyte.

Some of the yellow-brown anolyte was poured into a large volume of cold water at 15° C. The result of the hydrolysis was a red-brown powder, which was washed for a considerable time until the washings gave no precipitate with $BaCl_2$. It was then dried in a vacuum desiccator over conc. H_2SO_4 for 80 hours. It was completely soluble in cold dilute HCl. This solution gave a small quantity of precipitate with $BaCl_2$, but when the powder was heated with conc. HCl no chlorine was evolved. There was, therefore, sulphate present, but no persulphate.

The powder heated alone gave gold, oxygen, and water and a small quantity of SO_3. The gold to oxygen ratio was found. It was (*a*) 8·31, (*b*) 8·29, giving a mean 8·30—the ratio for hydrated $Au_2O_3 = 8·22$.

It is possible that the gold goes into solution in the trivalent and also in the monovalent state and that the product of hydrolysis contains a mixture of hydrated Au_2O_3 and of Au_2O. The ratio found corresponds to $Au_2O/Au_2O_3 = 0·01$. The presence of sulphate may be due to a basic auric sulphate, and the difficulty of washing free from sulphuric acid may be due to the slow hydrolysis of this basic sulphate when left under water.

The formation of finely divided gold distributed throughout the anolyte may be due to the transformation of an aurous compound in solution to an auric compound and gold ; this may account likewise for the free gold which separates when the anolyte is kept in a closed flask.

(ii.) A less concentrated acid was used as electrolyte, formed from 1 c.c. conc. H_2SO_4, density 1·84, diluted with 7 c.c. water.

The same acid was used for anolyte as for catholyte. The current was 2 amperes and the anode area $2 \times 6·84$ cm.^{2}.

The anolyte became of a pale-green colour, due to the formation of a gold compound ; the anode was covered with a deposit of brown solid, which flaked off into the liquid. The cathode remained bright without a trace of gold. There was no free gold in the anolyte. After washing for three weeks the brown powder was dried over conc. H_2SO_4 in a vacuum desiccator.

On heating it gave gold, oxygen, and water containing H_2SO_4. It was completely soluble in cold dilute HCl, and this solution gave a small quantity of white precipitate with $BaCl_2$; no chlorine was evolved on heating the powder with conc. HCl.

The mean value of the gold to oxygen ratio was 8·32.

The brown solid dissolved in cold conc. H_2SO_4 diluted with an equal volume of water, giving a green solution like the green anolyte in (i.) ; this green solution, when electrolysed with platinum anode and platinum cathode surrounded by a porous pot containing dilute H_2SO_4, was decomposed, giving a deposit of pure gold on the anode—there was no trace of gold on the cathode. The compound formed by this solution must therefore contain the gold as complex anions. The brown solid was left under a large quantity of $KHCO_3$ solution at room temperature for 13 weeks. Part of the solid was dissolved, giving a yellow solution, from which yellow crystals were obtained by allowing the solution to evaporate in a vacuum desiccator over conc. H_2SO_4. The residue was a dark purple solid, which when washed reacted with dilute HCl giving $HAuCl_4$ and gold.

It therefore appears that the brown powder is a mixture of hydrated auric oxide and Au_2O. The sulphate present is probably a basic auric sulphate which is slowly hydrolysed by water. The ratio found corresponds to $Au_2O/Au_2O_3 = 0·02$.

These results seem consistent with the hypothesis that a mixture of auric and aurous compounds is formed by the electrolysis with a gold anode, and that with an acid of this concentration the soluble complex gold compounds

cannot reach so high a concentration as in (i.), owing to the greater percentage of water present in the anolyte.

Orthophosphoric Acid Electrolyte.

The concentration of the acid used was approximately 15 per cent. H_3PO_4 by weight. The same concentration was used for the anolyte as for the catholyte initially, but during the electrolysis there was considerable transference of water from the anolyte to the porous pot. The level of the liquid in the pot had to be maintained constant by means of a capillary siphon, and to compensate the loss of water from the anolyte distilled water was arranged to flow into the anolyte so as to keep it at constant level.

The current used was 1 ampere, and the anode area was $2 \times 6{\cdot}84$ cm.^{2}.

No gold was deposited on the cathode. The anolyte was filtered, and on being concentrated by heating gave a small quantity of purple gold.

A brown solid was formed on the anode and flaked off into the beaker containing the anolyte. The anolyte remained colourless.

It appears, therefore, that the gold anode does not give rise to cations, but that a very small quantity of gold goes into solution as complex anions.

The brown solid was washed for about three weeks until water left on it for two hours gave no reaction with ammonium molybdate ; it was then dried over conc. H_2SO_4 in a vacuum desiccator.

When heated the solid gave gold, oxygen, and water which was slightly acid to litmus. The gold to oxygen ratio was determined by heating the solid and collecting the oxygen. It was 8·58.

The brown solid was completely soluble in cold dilute HCl. About 4 grams of the solid washed as described above were left in water and stirred, the water being frequently changed ; this was continued for 24 weeks. The water was tested every week for H_3PO_4 ; for long a precipitate was obtained with ammonium molybdate, the quantity of which decreased with successive changes of the water. Finally no trace of H_3PO_4 could be detected in the water.

The solid was dried over conc. H_2SO_4 in a vacuum desiccator and analysed. The gold to oxygen ratio was found to be (*a*) 8·62, (*b*) 8·60, giving a mean 8·61.

The water evolved on heating the solid was faintly acid to litmus.

It appears, therefore, that the quantity of the compound which gives H_3PO_4 with the water evolved on heating is a very small fraction of the total weight of solid, and that this compound is very difficult to hydrolyse completely.

About 3 grams of the solid was stirred continually with cold KOH solution. Nearly all the solid dissolved, but a small blackish residue insoluble in KOH solution was obtained. This with dilute HCl gave $HAuCl_4$ and gold ; it was therefore aurous oxide.

Hence the solid product at the anode consists of a mixture of hydrated auric oxide and aurous oxide ; the ratio 8·58 corresponds to $Au_2O/Au_2O_3 = 0{\cdot}07$.

An acid of concentration approximately 20 per cent. H_3PO_4 gave a solid of ratio 8·87, corresponding to $Au_2O/Au_2O_3 = 0{\cdot}09$.

In all cases where a porous pot was used to enclose the cathode, the outside of the pot was covered with a purple coloration where it was in contact with the anolyte. This purple coloration penetrated for a considerable distance into the wall of the pot when the pot had been used for a series of experiments. The purple coloration was due to gold. In order to see whether this could be caused by the action of the pot on the anolyte con-

taining complex gold ions independently of the current passing, an unused pot was broken and fragments left in beakers containing portions of the various anolytes. In all cases there was a deposition of purple gold. The same took place when the fragments had been previously heated red-hot so as to destroy any organic matter.

In these experiments with the gold anode the composition of the gold products formed does not seem to depend on the anode current density employed, but it is influenced by the concentration of the acid used for the anolyte. It was impossible to maintain this concentration constant, as the acid anions continually moved from the catholyte into the anolyte when the current was passing. In order to minimize the changes in concentration the volume of the anolyte used was large, and except in the cases of the nitric acid and sulphuric acid solutions which did not give solid gold compounds, the anolyte acid was changed after a few hours. In the cases of the nitric acid and sulphuric acid solutions which did not give any solid compounds at the anode, it was necessary to use the same anolyte acid continuously in order to observe the progressive colour changes.

The idea of experimenting with a gold anode was suggested to me by Colonel C. T. Heycock, M.A., F.R.S., Goldsmiths Reader in Metallurgy ; I am much indebted to him for his suggestion, and likewise for his kindness in giving me facilities for doing the work.

The University Chemical Laboratory,
Cambridge.

ON THE ELECTROLYSIS OF CONCENTRATED HYDROCHLORIC ACIDS USING A COPPER ANODE.

By F. H. JEFFERY, M.A.

(*A Paper read before the Faraday Society on Tuesday, October* 19, 1915. Sir Robert Hadfield, F.R.S., President, *in the Chair.*)

The apparatus was similar to that employed for the experiments with the gold anode, save that the beaker, porous pot, and electrodes were enclosed in a bell jar over water, so that the electrolysis might be performed in an atmosphere of nitrogen. The anolyte was stirred as previously.

The current used was 0·5 ampere. No copper was deposited on the cathode, nor was there any trace of copper compound in the catholyte after six hours' steady current.

The anolyte became slightly yellow and there was a considerable quantity of a fine blackish powder on the bottom of the beaker and on the anode. There was also a sediment of white powder. The black powder was found to be metallic copper, due to the disintegration of the anode.

The white powder was cuprous chloride. No chlorine was evolved during the electrolysis.

The anolyte gave a white precipitate of cuprous chloride on addition of water; with sodium hydroxide solution it gave a yellow precipitate of cuprous hydroxide; with ammonium hydroxide it gave a gradually deepening blue coloration on shaking in the air.

It appears, therefore, that the copper goes into solution as complex anions, and as excess of hydrochloric acid is present these are probably the ions corresponding to H_2CuCl_3.

As the CuCl was formed towards the end of the electrolysis it may be that this reaction is represented by $CuCl_3'' \rightleftarrows CuCl + 2Cl'$.

An alternative explanation would be that CuCl is formed directly from the chloridion and the copper anode, and that this dissolves without dissociation in the hydrochloric acid present until a saturated solution is formed, when there is precipitation of CuCl on the bottom of the beaker as the electrolysis proceeds.

In order to test this latter hypothesis the following experiment was made. Starting with pure concentrated hydrochloric acid and a clean copper anode, the electrolysis was performed for six hours with a steady current of 0·5 ampere. Then the current was stopped, but all other conditions, including the stirring, were maintained the same as when the current was passing. After three hours the catholyte was examined and it was found that some of the copper compound in the anolyte had diffused into the catholyte.

This could not have been prevented for six hours by the passage of the current unless the copper had been present as complex anion.

If the electrolysis was continued after some of the copper compound had diffused into the catholyte, copper was at once deposited on the cathode. This was due to the complex copper compound being reduced by the hydrogen at the cathode.

A similar series of experiments was performed using as anolyte a solution of 30 grams KCl per 100 grams water and as catholyte dilute HCl : during these experiments all manipulations were performed in CO_2. The copper went into solution entirely as anion ; there was no metallic copper scattered in the anolyte compartment from the disintegration of the anode and the anode could be weighed after an electrolysis. A voltameter was put in series with the cell and the hydrogen collected. The amount of copper going into solution per faraday was (i) 63·7, (ii) 63·6 grams. No chlorine was evolved. It was found possible to isolate a potassium salt corresponding to the complex anion by allowing some of the anolyte after an electrolysis of two hours with current 0·5 amperes to evaporate in a vacuum desiccator over conc. H_2SO_4. Crystals were obtained and analysed ; the copper was estimated electrolytically from an ammoniacal solution and the chlorine was weighed as AgCl from a solution in dilute HNO_3. The ratio Cu/Cl was found to be 0·335 ; for K_2CuCl_3 this ratio is 0·333. It appears therefore that the complex anion is $CuCl_3''$. As in the case of conc. HCl, CuCl was precipitated when the electrolysis was prolonged.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

THE CORROSION OF METALS: FERROUS AND NON-FERROUS

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Wednesday, December 8, 1915, at the Institution of Electrical Engineers, Victoria Embankment, London, W.C., a **General Discussion** on **The Corrosion of Metals, Ferrous and Non-Ferrous,** took place. **Sir Robert Hadfield, F.R.S., President,** was in the chair.

INTRODUCTORY ADDRESS ON THE CORROSION OF STEEL ALLOYS.

By Sir ROBERT HADFIELD, F.R.S.

The Proceedings were opened by the **Chairman,** who delivered the following Introductory Address.

In the presentation of this symposium of papers on the interesting subject of "Corrosion" it can be quite correctly stated that there is no more important subject than this study of man's fight against Nature, whether on land or sea. It has been estimated that the losses of the iron in the world by corrosion amount to hundreds of thousands of tons annually. Man at great pains smelts the iron ore taken from Mother Earth and produces what is termed "metal." Nature immediately sets to work to destroy man's handiwork, and, except in certain favoured spots of the world, she generally conquers; at any rate, this is so in our Northern climes. It is true that in the drier parts of our world, such as Egypt, where the amount of moisture is very small, Nature is more lenient in her treatment of the metal ferrum and its compounds known as iron and steel. For example, Professor Flinders Petrie, F.R.S., has been kind enough to lend the author to exhibit to-night an Egyptian hatchet of iron, also other articles. The hatchet possesses a bright scale over the greater portion of its two sides, and is apparently in exactly the same state as when it left the forge. It shows no trace of rust or other evidence of faults in the material. This hatchet is vouched by Dr. Flinders Petrie, our leading Egyptologist, as being at least 2,500 years old. A double axe also shown, which is about 10½ in. in length, was a little later date, 400 B.C.; two other hatchets, 700 B.C.; a small knife, 700 B.C.; and a large knife, provided with a cast bronze handle, about 800 B.C.

In a general way it may be stated that the following are the types of corrosion usually met with:—

(*a*) Corrosion from ordinary atmospheric effects.

(*b*) Corrosion from special atmospheric conditions—for example, in manufacturing centres, where the air is less pure.

(*c*) Corrosion in special media such as gases, acids, or other liquids.

(*d*) Corrosion by heating effects. This is usually termed oxidation, but it is, of course, more or less corrosion.

Losses by rust, oxidation, and even erosion may all be considered part of the same genus "corrosion," that is, the results obtained from each of the types named are governed by the same or, at any rate, similar laws.

Studies of the alloys of iron by which corrosion can be governed or corrected and conclusions arrived at as to the kind of alloys, whether of iron or other metals, which best resist this deterioration are to be encouraged, and should be of great service to mankind.

Any of us who can, therefore, add to the life of iron and steel in its forms and uses will be a public benefactor, and although the present supplies of iron in the world are of enormous variety and extent, a time will eventually come when probably the iron of the world will have to be more carefully husbanded than now, when evidence of much waste of the metal is rife on every hand.

The old proverb that "He who owns the iron of the world will rule the world" is being exemplified in the terrible struggle now taking place. It is, indeed, a war of "iron," and the thunderbolts wielded by Jove were trifling compared with modern engagements on land and sea. All of us, whether friend or foe, must yearn for the happier times when the metal iron, to whose qualities we metallurgists bow down in the many fascinating studies it presents to us, will once more be used only in the arts of peace.

The contributors this evening represent those who have carried out special investigations on this important question of corrosion and corrodibility, especially with regard to iron and steel.

We have to-night excellent papers by Dr. J. Newton Friend; by Dr. C. H. Desch; by Mr. Leslie Aitchison, one of Dr. Arnold's demonstrators in the Applied Science Department of the Sheffield University who has submitted a most thorough and exhaustive paper on his researches, and in connection with which Part I of his paper read before our Society in May last should be considered; also by Messrs. Whyte, Gibbs, Philip, and others.

We are much indebted to each one of these authors for the trouble they have so kindly taken in presenting the results of their interesting labours, specially in this time of national stress when our thoughts are so much engaged in sterner matters.

It may be added that at the present time Dr. J. Newton Friend, from whom this evening we have a most interesting paper, and the author are engaged on several important researches on the corrosion of a large number of different kinds of steel and its alloys. We are submitting specimens comprising most of the special alloys the author has produced during the last twenty years, to a full and exhaustive examination as to their corrosive qualities, the results of which we hope before long to give to one of the scientific Societies.

Exaggerated claims were made a few years ago that nickel steel would resist corrosion. No doubt if the metal is present in high percentages the product is more highly resistant, but in the end it will also corrode, and quite badly. Moreover, as regards ordinary commercial nickel steels of lower percentages, whilst they show somewhat lower corrosion, it is found that, when deterioration once commences, corrosion continues at not much less rate than in ordinary steel.

The late Mr. T. Andrews, F.R.S., made many exhaustive researches on this subject, some of them abstruse, perhaps, but those who are interested in this matter can with advantage refer to his work.

A special alloy known as "Stainless Steel" has recently come before the metallurgical world.

Great credit is due to Messrs. Thomas Firth & Sons, to Mr. H. Brearley and others for the work they have done in this matter.

In this connection reference may be made to some experiments by the author of this communication, carried out in 1892. In his paper on "Alloys of Iron and Chromium," read before the Iron and Steel Institute in 1892, it was pointed out that an alloy containing about 9·18 per cent. of chromium and ·71 per cent. of carbon showed a loss of 5·64 per cent. after being immersed for 21 days in sulphuric acid of 50 per cent. volume, compared with 4·47 per cent. loss of wrought iron. The following table gives the data :—

TABLE I.

Mark of the Specimen in the Hadfield research.		Percentage of		Strength of Acid (H_2SO_4).	Length of Immersion	Loss per cent.	Colour after Treatment.
		C.	Cr.	%	Days.		
Chromium steel (F)	Bar	·27	1·18	50	21	3·32	Bright appearance in some parts.
Chromium steel (J)	Bar	·77	5·19	50	21	4·78	Tarnished, no bright appearance.
Chromium steel (L)	Bar	·71	9·18	50	21	5·64	Dull and tarnished.
			Si.				
Silicon steel (E)	Bar	·20	2·67	50	21	3·32	Very bright appearance.
Ordinary mild steel	Bar	—	—	50	21	7·48	Dull bright.
Wrought iron	Bar	—	—	50	21	4·47	Most brilliant.

The above Table I shows the results of the corrosion tests, and Table II of the mechanical tests. Each sample, 2½ in. × ½ in. × ¼ in., was immersed for 21 days in H_2SO_4 of 50 per cent. strength. The samples "F" (1·18 per cent. Cr.), "J" (5·19 per cent. Cr.) "L" (9·18 per cent. Cr.) showed a loss of 3·32 per cent., 4·78 per cent., and 5·64 per cent. respectively. Ordinary mild steel, tested under the same conditions, lost 7·48 per cent. and wrought iron 4·47 per cent.

On recently referring to a number of the test bars prepared in 1892, and tested in connection with the research above mentioned, it was found that the specimens containing the percentages of chromium in question, and particularly specimens Nos. 1176M and 1177M, were on the whole quite bright and practically free from rust. This specially applied to No. 1177M, further information regarding which is given later on in these remarks.

The foregoing is remarkable confirmation of the importance of chromium in this particular percentage combined with iron, conferring

upon such an alloy practically freedom from ordinary rust or corrosion properties compared with ordinary iron and steel.

No special care was taken with the test bars in question. They were filed away in our research laboratory in Sheffield and had never been touched during this interval of time, namely, about 23 years.

The following Table II shows the data with regard to these particular specimens Nos. 1176M and 1177M:—

TABLE II.

Specimen No.	Analysis. C.	Si.	S.	P.	Mn.	Cr.	Treatment.	Tensile Tests. Elast. limit. Tons.	Max. load. Tons.	Elong. %	Reduction of Area. %	Bending test.
1176M.	1·27	·38	·10	·03	·25	11·13	Unannealed.	30 to 35	62	10	11	24° broken.
							Annealed for four days at a high red.	Bar began to crack in thread at 5 tons up to breaking at 33 tons.				14° broken.
1177M.	1·06	·63	·12	·06	·08	10·83	Unannealed.	35 to 40	72	5	5	nil broken.
							Annealed for four days at a high red.	26	56	12	12	68° broken.

The tensile bars above mentioned, which were prepared on the 24th September, 1890, were examined on the 12th March, 1915.

Steel No. 1176M.—The unannealed is still bright, except for a patch of rust on one side. The fracture is slightly rusted.
The annealed bar is similar.

Steel No. 1177M.—The unannealed bar is mostly quite bright, but there are fairly large patches of rust. The fracture is completely rusted.
The annealed bar is only very slightly rusted in places. The fracture is completely rusted.

It will be thus seen that the author produced an alloy of iron and chromium offering great resistance to corrosion, and somewhat similar to the "Stainless" steel previously mentioned.

With reference to the interesting material of the kind to which the term "Stainless" has been given, Table III gives the analysis and mechanical tests carried out by the author on similar material made by him. It will be noticed that the carbon is much lower than in the chromium iron alloys produced by him in 1892.

This new steel, which has been used for table cutlery, is stated to neither rust nor tarnish in contact with food or acids. It is now making great headway. The author believes that cutlery manufacturers are making use of it on quite a large scale, for, although the cost is considerably more than knives made from ordinary steel, it is much superior in its anti-corrosive qualities.

A short time ago the author had some interesting correspondence with Sir John Wolfe Barry, F.R.S., who asked him what he considered to be the value of this high chromium steel as to its practical application, and whether it could be used for parts of dock gates and other purposes, where corrosion is very considerable ; also could it be produced in the form of plates, angles, and other products.

In Table III will be found a considerable number of mechanical tests on this particular steel. The elastic limit and tenacity vary according to the heat treatment.

The elastic limit of the forged material is high, varying from 28 to 33 tons per square inch, breaking load 44 to 50 tons ; the elongation is excellent when the material is annealed, being as high as 27 per cent. on 2 in., with a reduction in area of 50 per cent. The ball hardness in this case is 185.

As shown in the Table, a forged bar of this material after being annealed would give a drop tup test of no less than 29 Kg. (Frémont system) with a bending angle of 104° before breaking.

The material requires considerable care in forging and rolling, but there is no doubt an important opening could be found for this valuable product, of which probably this present paper is the first to put before the world full and detailed information as regards its composition and mechanical qualities.

Rather singular to say this steel does not show satisfactory corrosion resistance in 10 per cent. sulphuric acid solution. The alloy steel containing 10 per cent. shows a loss of 18 per cent., and that with 15 per cent. chromium a loss of no less than 33 per cent. This is excellently shown in Tables V and VI, also Fig. 13 of Mr. Aitchison's paper, Part I, on "Experiments on the Influence of Composition on the Corrosion of Steel," read before this Society in May last. In my own laboratory these tests have been confirmed. It would therefore be well, in order to determine whether high chromium steels are adapted for resisting corrosion—for example of, say, sea-water for parts of dock gates and elsewhere—that full and proper tests should be first carried out, for example, in sea-water and other media.

The author, in order to determine the corrosion of the metal chromium itself, experimented with a number of specimens of metallic chromium containing 99·35 per cent. chromium. The results show that this metal is readily soluble in dilute and strong hydrochloric acid ; insoluble in dilute and strong nitric acid ; soluble and slightly soluble in dilute and strong sulphuric acid.

To this information may be added the following interesting data, which, as far as the author is aware, has not yet been put before the world in any previous records.

The metallic chromium would not forge at low or bright red heat ; it was not attracted by magnet. After heating to bright red heat and quenching in water, it was still not attracted by magnet. The hardness was about the same as before the treatment ; that is, in all cases the metallic chromium was fileable.

Not long ago the author carried out in collaboration with the well-known American scientist, Dr. Allerton S. Cushman, who has made such a long and exhaustive study of corrosion tests, the following

TABLE

MECHANICAL TESTS ON STEEL OF

Steel No.	Analysis.						Treatment.	Tensile	
	C.	Si.	Mn.	Cr.	Co.	Fe.		E.L. tons.	B.L. tons.
							OUTSIDE MATERIAL.		
2498	·28	·01	·12	12·7	·45	86·6	Blade bent through	angle	of abt.
2498A	·35	—	—	—	—	—	775° (F.) † ..	—	—
							MATERIAL MADE BY HADFIELD.		
3432	·35	—	—	11·66	—	—	Cast 1100° Air	14·5	37·6
							775° (F.)		
							Forged 775° (F.)	28	44·5
3433	·41	—	—	10·14	—	—	Cast 1100° Air	34	51·4
							775° (F.)		
							Forged 775° (F.)	33	49·4
3433-2	·29	—	—	12·84	—	—	Cast 1100° Air	14½	34·6
							775° (F.)		
							Forged 775° (F.)	27·5	42·3

† "F" = cooled in furnace.

III.

THE TYPE KNOWN AS "STAINLESS."

Test.		Shock Test.				—	Ball Test.	Corrosion Test.
		"C" nick.		"No" nick.				21 days in 50% solution of H_2SO_4.
Elong. %	R.A. %	Kgm.	Angle.	Kgm.	Angle.			Loss in grs. per sq. cm.
25°	before	breaking.				Scleroscope. 32-80 Too thin for test. Easily able.	Mohs. 6 ball file-	
—	—	4·7	12°	—	—		255 on shock, 600 on bar as received.	
							On Shock	
29·5	54·9	2·6	6°	42	115°		163	
27	51·6	5·1	16°	29	104°		185	
						**Ball Tests.*		
12	13·7	2·6	5°	7	18°	*Ingot.* cast. / *Bar.* As fgd	228	
13	26·7	3·5	10°	31	As 78°	600 / 645.	212	As forged ·046
						1100° Air 645		775° (F.) ·037
32·5	59·3	3·1	10°	54	127° Unbr.		146	
29	61·5	12·5	44°	51	135°		177	

* Further ball tests on steel No. 3,433. The samples were ½ in. sq. × 1½ long (1-16 in. ground off surface).

			Hardness Number.
775°	quenched in	Oil ..	328
775°	,,	Water	328
830°	,,	Oil	321
830°	,,	Water	324

experiments, of which particulars are now given for the first time. The observations by Dr. Cushman are given in Table IV, and the joint results by Dr. Cushman and the author in Table V. The specimens furnished to Dr. Cushman by the author are identical with those upon which his own research was carried out, the immersion being for 20 days in 50 per cent. sulphuric acid. Dr. Cushman's tests as regards the 50 per cent. sulphuric acid test do not altogether agree with the author's. There is, however, fairly close agreement as regards the tests made in acid of 25 per cent. strength.

Table IV.

Representing Dr. Cushman's Tests.

Dr. Cushman states:—

"I have completed in my laboratory a number of the acid tests on the various specimens of steel which you sent me, according to the method which I have always used in carrying out the acid test."

Results of Tests on seven samples of Hadfield Steels by Immersion in Sulphuric Acid.

Strength of Acid, 20 per cent. Sp. gr., 1·144 at 15° C.
Temperature, 20° C.
Time of Immersion, 1 hour.

Mark.	Size of specimen. Inches.	Original Weight.	Loss. Grms.	Area. Sq. cm.	Grms. per sq. cm.	S.C.I. = 100.
2228	2 × ½ × 1-16	7·7714	·0632	14·91	·0042	125
1795	2 × ½ × 3-64	5·7874	·0387	14·41	·0027	76
2020L	2 × ½ × 1-16	7·1224	·0654	14·91	·0044	129
S.C.I	2 × ½ × 1-16	6·7825	·0506	14·91	·0034	100
1618/2	2 × ½ × 1-16	6·5923	·0622	14·91	·0042	125
2228	2 × ½ × 1-16	8·0311	·0622	14·91	·0042	125
2229..	2 × ½ × 1-16	7·1354	·0537	14·91	·0036	106

Average Loss on Various Steels.

3% Nickel steel	·0195
20% ,, ,, ...	·0062
25% ,, ,, ...	·0012
30% ,, ,, ...	·0010
Chrome steel	·0400
Chrome Vanadium steel	·0285
Nickel Chrome steel	·0170
,, ,, ,, ...	·0230
13% Tungsten steel	·0500
10% ,, ,, ...	·0420
Silico Manganese Vanadium steel	·0400

The composition of these steels is shown in Table V, giving the author's corrosion experiments on the same steels.

TABLE V.

Representing the Hadfield Tests Compared with those of Dr. Cushman.

No.	Analysis %.					Heating and Cooling Treatments.	Cast or Forged.	Dr. Cushman's Tests.		Hadfield's Tests.			
								20% Acid. 1 hour at 20° C.		25% Acid. 1½ hours.	50% Acid. 20 and 21 days.		
	C.	Si.	Mn.	Cr.	Ni.			Loss per sq. cm., grms.	% Loss. S.C.I. = 100.	Loss per sq. cm., grms.	Loss per sq. cm., grms.	% Loss. S.C.I. = 100.	
S.C.I..	—	—	—	—	—	970° W., 560° W.* ..	Forged	·0034	100	—	·0492	100	
1618–2	·54	·16	1·03	—	—	940° Oil, 615° W. ..	Cast .	·0042	125	·0105 ·0124	·0763	155	
1795C	·30	—	·40	1·81	3·47	1050° Air, 745° F.† 745-660° W., 580° W., 580° W., 580° W., 615° W., 745-660° W., 615° W., 615° W.	Cast .	·0027	76	·0096	·0474	96	
2020L	·28	·19	1·40	—	—	940–505, 725° F.	Cast .	·0044	129	—	·0432	88	
2228 .	·52	·05	·06	—	—	1100° Air, 775° F. ..	Cast .	·0042	125	·0162	·0464 ·0250	94 51	72
2228 .	·52	·05	·06	—	—	940° Oil, 615° W. ..	Cast .	·0042	125	·0120 ·0159	·0532 ·0361	108 73	90
2229 .	·29	·31	·48	—	—	900° Oil, 790° F., 540° F.	Forged	·0036	106	·0103 ·0132	·0358	73	

* " W " = quenched in water from the temperatures given.
† " F " = cooled in furnace from the temperatures given.

The author has carried out from time to time on various steels a considerable number of researches with regard to corrosion tests. These are shown in Table VI. The test consisted of immersing the specimens for 21 days in a 50 per cent. volume solution of sulphuric acid.

In addition to the foregoing the author has made a large number of corrosion tests as shown in Table VII. and referred to in his various papers during the last 25 years on Alloys of Iron, to which have been added the following special elements :—

(*a*) Nickel.
(*b*) Tungsten.
(*c*) Chromium.
(*d*) Silicon.

In Diagram I are plotted the various results shown in Table VII.

An interesting Table, VIII, is also added, relating to the author's research experiments No. 5,667, showing the corrosion on ordinary carbon steel ; manganese steel ; chromium nickel ; manganese chromium nickel steel ; chromium nickel steel ; and manganese nickel steel.

In Table IX will be found a list of the exhibits accompanying this paper.

In conclusion, the author trusts that these remarks may be of some service in contributing further knowledge to the interesting subject of Corrosion, as presented in this valuable series or symposium of papers to-night.

TABLE VI.—*Corrosion Tests on Various Steels for Comparison with High Chromium Steels.*

All specimens were immersed for 21 days in a 50 per cent. volume solution of Sulphuric Acid.

Steel No.	Analysis. C.	Si.	Mn.	Cr.	Ni.	W.	Cu.	Cast or Forged.	Treatment.	Corrosion % Loss.	Corrosion. Loss in gms per sq. cm.
2239 American Ingot Iron	·03	·01	·015	—	—	—	—	Forged	As received.	1·96	·0152
2235	·31	—	·06	—	—	—	—	Cast	895 O.* 790 F. 540 F.†	9·06	·0647
								Forged	895 O. 790 F. 540 F.	6·30	·0450
2020 L.	·28	·19	1·40	—	—	—	—	Forged	940 O. 615 W.§	9·95	·0710
											Repeat
2228	·52	·05	·06	—	—	—	—	Forged	940 O. 615 W.	9·23	·0658
											Repeat
1618	·52	·09	·62	—	—	—	—	Forged	940 O. 615 W.	7·90	·0564
1991/2	·97	·11	·13	—	—	—	—	Cast	940 O. 615 W.	7·25	·0517
								Forged	940 O. 615 W.	8·35	·0595
1905	·76	—	·95	—	—	—	—	Forged	940 O. 615 W.	7·40	·0528
2054	·29	·29	1·17	·81	—	—	—	Cast	970 W. 560 A.‡	7·51	·0536
								Forged	970 W. 560 A.	7·00	·0714
2231	·30	·21	1·44	·56	2·10	—	—	Forged	830 O. 615 W.	7·25	·0517
2232	·25	—	—	—	—	2·13	—	Cast	830/680 W. 725 F. 615 W.	7·10	·0507
2001	·44	·09	·35	—	—	3·51	—	Cast	940 O. 615 W.	5·89	·0420
								Forged	940 O. 615 W.	8·40	·0600
2222	·26	—	·34	—	3·44	1·65	—	Forged	As forged	6·84	·0488
1498	·84	—	·07	—	2·04	2·10	—	Cast	830/680 W. 725 F. 615 W.	7·05	·0503
2233	·28	—	·95	—	1·94	2·78	—	Forged	830 O. 615 W.	2·75	·0199
1773 J.	·35	·10	·33	2·82	—	18·90	—	Forged	725 F.	6·35	·0454
1957	·26	·21	·44	—	—	—	1·08	Forged	1000 A. 775 F.	3·85	·0275
SPECIAL STEEL CONTAINING HIGH PERCENTAGE OF CHROMIUM.											
1177 M.	1·06	·63	·08	10·83	—	—	—	Forged	As forged	5·62	·0380
3433	·41	—	—	10·14	—	—	—	Forged	As forged	6·44	·0460
3433	·41	—	—	10·41	—	—	—	Forged	775 F.	5·18	·0370

* "O" = quenched in oil. † "F" = cooled in furnace. § "W" = quenched in water. ‡ "A" = cooled in air.

TABLE
Corrosion

Specimen.	Analysis %							
	C.	Si.	S.	P.	Mn.	Ni.	Cr.	W.
A	·47	—	—	—	·95	—	—	—
B	·48	—	—	—	·75	1·20	—	—
C	·47	—	—	—	·86	2·15	—	—
D	·40	—	—	—	·82	4·25	—	—
E	·42	—	—	—	1·03	4·95	—	—
F	·52	—	—	—	·92	6·42	—	—
G	·43	—	—	—	·79	7·95	—	—
H	·41	—	—	—	·85	12·22	—	—
J	·45	—	—	—	·83	15·98	—	—
K	·41	—	—	—	·96	19·91	—	—
B	·15	—	—	—	—	—	—	·20
G	·21	—	—	—	—	—	—	1·49
H	·28	—	—	—	—	—	—	3·40
I	·38	—	—	—	—	—	—	7·47
L	·76	—	—	—	—	—	—	15·65
M	·78	—	—	—	—	—	—	16·18
Ordinary Steel	·40	—	—	—	·80	—	—	—
Mild Streel	·25	—	—	—	—	—	—	—
Nickel-iron Alloy	·16	—	—	—	—	24·51	—	—
Platinoid	—	—	—	—	—	—	—	—
Metallic Chromium	—	—	—	—	—	—	98·0	—
Metallic Manganese	—	—	—	—	99·0	—	—	—
Nickel	—	—	—	—	—	98·50	—	—
Iron	—	—	—	—	—	—	—	Fe. 99·80
Chromium Steel F	·227	—	—	—	—	—	1·18	—
,, ,, J	·77	—	—	—	—	—	5·19	—
,, ,, L	·71	—	—	—	—	—	9·18	—
Silicon Steel E	·20	2·67	—	—	—	—	—	—
Mild Steel	—	—	—	—	—	—	—	—
Wrought Iron	—	—	—	—	—	—	—	—
1287 C	·13	·23	—	—	·72	·95	—	—
,, E	·19	·20	—	—	·65	3·82	—	—
,, G	·17	·28	·11	·08	·68	7·65	—	—
,, I	·18	·22	—	—	·93	11·39	—	—
,, M	·14	·38	—	—	·86	29·07	—	—

These results, representing corrosion tests carried out by Hadfield during the last twenty-three years, are plotted together in Diagram I, which accompanies this paper.

VII.

Tests.

Condition of Material.	After 32 Days in Water.	After 33 Days in Sea Water.	After 17 Days in 50% H_2SO_4.	After 21 Days in 50% H_2SO_4.		
	Loss %	Loss %	Loss %	Loss in Grams.	Loss %	
Forged	·15	—	·80	—	—	Particulars of these are taken from the Author's joint paper on "Iron, Nickel, Manganese, Carbon Alloys," read before the Institution of Mechanical Engineers in 1905.
,,	·11	·23	1·10	—	—	
,,	·10	·26	·72	—	—	
,,	·11	·26	·71	—	—	
,,	·12	·24	·66	—	—	
,,	·12	·23	·58	—	—	
,,	·12	·23	·54	—	—	
,,	·10	·23	·44	—	—	
,,	·09	·18	·28	—	—	
,,	·09	·14	·28	—	—	
Forged	—	—	—	3·055	5·01	Extracted from the Author's paper on "Alloys of Iron and Tungsten," read before the Iron and Steel Institute in 1903.
,,	—	—	—	2·162	3·50	
,,	—	—	—	1·392	2·25	
,,	—	—	—	2·797	4·50	
,,	—	—	—	3·920	5·75	
,,	—	—	—	3·574	5·50	
,,	—	—	—	—	3·97	
,,	—	—	—	—	2·09	
Cast	—	—	—	—	1·37	"The loss noticed did not differ greatly from those met with in the tests on iron, manganese, silicon, aluminium, chromium and nickel alloys. They are somewhat more than on nickel steel."
—	—	—	—	—	·35	
—	—	—	—	—	·03	
—	—	—	—	—	10·60	
—	—	—	—	—	very slight	
—	—	—	—	—	4·52	
Forged	—	—	—	—	3·32	Extracted from the Author's paper on "Alloys of Iron and Chromium," read before the Iron and Steel Institute in 1892.
,,	—	—	—	—	4·78	
,,	—	—	—	—	5·64	
,,	—	—	—	—	3·32	
,,	—	—	—	—	7·48	
,,	—	—	—	—	4·47	
Cast	—	—	—	2·003	3·23	Extracted from the Author's paper on "Alloys of Iron and Nickel," read before the Institution of Civil Engineers in 1899. These samples were immersed for 21 days in 50% H_2SO_4.
,,	—	—	—	1·611	2·95	
,,	—	—	—	1·581	2·77	
,,	—	—	—	1·390	2·60	
,,	—	—	—	·759	1·34	

TABLE VIII.

Experiment No. 5667.

Size of Specimens { 4 in. × ⅞ in. × ⅛ in.
{ 10·16 × 2·2225 × ·3174 c.m.

Steel No.	Analysis %					Weight.			Loss per sq. cm.	Percentage loss. %
	C.	Si.	Mn.	Cr.	Ni.	Before Corrosion, grms.	After Corrosion, grms.	Difference.		
6	·39	·55	·93	—	—	41·407	39·977	1·430	·0270	3·45
1010	1·20	—	12·14	—	—	43·460	42·144	1·316	·0248	3·03
628	1·26	·70	13·79	2·07	—	46·080	45·712	0·368	·0069	0·821
1563	1·50	—	12·75	—	1·92	38·762	37·406	1·356	·0256	3·50
1481	1·55	—	11·36	2·06	2·04	44·400	42·925	1·475	·0278	3·32
1798K	·59	—	1·01	—	22·80	48·030	47·695	0·335	·0063	0·695
1795	·31	—	·29	1·80	3·47	48·010	47·100	0·910	·0172	1·895
1109 D	·60	·84	5·04	—	14·55	42·760	42·133	0·827	·0156	1·935

TABLE IX.

DESCRIPTION OF THE SPECIMENS ACCOMPANYING THIS PAPER EXHIBITED BY SIR ROBERT HADFIELD.

Chromium Steel.	Specimens used in the determination of the corrosion properties of Chromium Steels as given in Hadfield's paper on "Alloys of Iron and Chromium," read before the Iron and Steel Institute in 1892. These are referred to in Table I of the present paper.
Ancient Iron.	Chippings from the ancient wrought Iron Pillar at Delhi. This Pillar was probably made about the Fourth Century A.D. A feature of this remarkable Pillar is the resistance it has offered to atmospheric corrosion extending over a period of more than 16 centuries; also an Egyptian Axe and other Iron tools about 2,500 years old, kindly lent for the evening by Dr. Flinders Petrie, F.R.S. All these specimens have shown great resistance to Corrosion.
American Ingot Iron.	A highly decarbonized and purified Iron made by the open-hearth process. This material has good anti-corrosion qualities, said to be due to the low Manganese content, and has been largely used in America for structures exposed to corrosive influences. Loss in 25 per cent. Sulphuric Acid in 1½ hours equals 5·7 milligrams per square cm.
English Ingot Iron.	This product is similar to that known as American Ingot Iron—that is, it is applied for anti-corrosion purposes. Loss in 25 per cent. Sulphuric Acid in 1½ hours equals 18·7 milligrams per square cm.
Nickel-Chromium-Iron Alloy.	This alloy has a very high electrical resistance, and is practically unattacked by acids. Electrical resistance, 104 microhms per c.c.
Iron-Nickel-Copper Alloy.	Made with Nickel Copper Alloy, prepared from Nickeliferous Copper Ore by C. H. Clamer, Philadelphia. This material is said to have shown excellent anti-corrosive properties when used as roofing sheets.
Ferro-Silicon.	This material has been largely used for the linings of vessels and conduits in the manufacture and storage of acids.
Cobalt-Chromium Alloy, known as "Stellite," and made by E. Haynes, Indiana, U.S.A.	The articles made from this alloy possess a fair cutting edge, and resist the attack of acids. For this reason the material is used for Cutlery and other purposes. A small pocket knife was exhibited. The alloy is non-magnetic. Loss in 25 per cent. Sulphuric Acid in 3 hours equals 1 milligram per square cm.
High Chromium Iron Alloy of the type known as "Stainless" Steel.	Table knife made from Chromium Iron Alloy.
"Tantiron" Non-Corrodible Cast Iron.	This material is stated to be absolutely non-corrodible by commercial acids.
"Toncan" Anti-Corrosive Steel.	Various specimens.

PHYSICAL AND MECHANICAL FACTORS IN CORROSION.

Dr. Cecil H. Desch, Graham Young Lecturer in Metallurgical Chemistry in the University of Glasgow, contributed to the Discussion the following Paper on "Physical and Mechanical Factors in Corrosion."

It is generally recognized that the corrosion of a metal or alloy is intimately connected with the formation of local electrolytic couples at the surface in contact with the solution or atmosphere. The process of corrosion is always initially one of chemical solution, the dependence of which on electrolytic conditions is established. A highly purified specimen of zinc is almost inactive towards acids, whilst commercial zinc, containing lead, is rapidly attacked, the action of the acid beginning in the immediate neighbourhood of the lead particles. This is one of a large class of similar facts, the bearing of which on the question of corrosion is often overlooked. The object of the present Paper is to show how the mechanical heterogeneity of metals and alloys affects the nature and velocity of the process of corrosion.

Laboratory tests of corrodibility are commonly made for the purpose of determining which of several materials will offer the greatest resistance to corrosion when exposed under certain specified conditions. As it is impracticable to reproduce these conditions exactly, on account of the long duration of the tests, rapid tests, involving the use on the one hand of active chemical corroding agents, or on the other of an applied electromotive force, are commonly adopted. Such tests are usually of an unsatisfactory character. A number of metals or alloys, arranged in order of their resistance to acid solutions, will present a very different order when exposed to technical conditions, such as contact with town air or sea-water.

Moreover, tests which involve the determination of the weight of material removed by the corroding agent, usually including that which is removed by brushing or scraping after corrosion, confound a number of successive changes in such a way that their separate influences cannot be disentangled. For example, experiments which determine the relative loss of weight of specimens immersed in an acid or salt solution for equal periods of time fail to distinguish between (*a*) the material actually dissolved and remaining in solution, (*b*) the loose, flocculent precipitate of basic salts which is produced in salt solutions, (*c*) the adherent film of basic salts which in some cases has the properties and effect of a tough, protective varnish, (*d*) the metallic layers, such as the spongy layer of copper formed in the "dezincification" of brass, and (*e*) crystals mechanically dislodged from the face of the specimen by solution of the material surrounding them. All these five products are removed when the specimen is brushed or scraped before re-weighing, but their relative quantity is not determined, although the power of a metal or alloy to resist corrosion depends in no small measure

on the ratio between these quantities. From an examination of the surface after an experiment of this kind, the corrosion is described as "general corrosion" or as "pitting," the latter referring to localized attack, the solution of the metal being either entirely limited to, or greatly intensified in, definite areas. Microscopical examination, however, often shows that what is apparently general corrosion is really pitting on a minute scale. An annealed α brass exhibits true general corrosion, the surface being uniformly attacked, except that neighbouring crystal grains of different orientation may show slight differences of level. On the other hand, a light aluminium alloy corrodes by minute pitting, the pits bearing a definite relation to the arrangement of the micrographic constituents.

The heterogeneity which gives rise to the formation of local couples may be of two kinds, chemical or physical. A pure metal is of necessity chemically homogeneous in the sense that it is made up of only one kind of atoms, but it may be physically heterogeneous. A metal which has been "cold-worked," or deformed at a temperature below that at which complete recrystallization takes place, contains, as shown by Dr. Beilby, films of amorphous material between the separate crystal grains. The amorphous metal is more electro-positive than the crystalline, as is shown by measuring the difference of potential between two specimens of the same metal in the cold-worked and annealed state respectively.* Consequently, cold-rolled metals almost always corrode in such a way that greater chemical action takes place along certain lines than along others, such lines following the direction of the rolling. This effect is not to be confused with the striation observed on the surface of rolled plates due to the inclusion of impurities. Rolled sheet-iron will corrode in parallel lines even in the absence of cold-working, on account of the presence of particles of scale which are embedded in the surface during rolling and produce a heterogeneous structure. Cold-worked metals become striated during corrosion, however, even when the outer skin has been completely removed before the test was made. Fig. 1 shows the corroded surface of a specimen of rolled duralumin, in which the lines of rolling are clearly indicated.

There are thus two reasons for the greater corrodibility of cold-worked than of annealed metals: the more electro-positive character of the former, and their greater heterogeneity. Against this must be set the fact that some metals are commonly porous in the cast or annealed state, and that the closing of the surface pores by cold-rolling may increase the resistance to corrosion, in some cases more than compensating in this way for the electrochemical difference. This applies mainly to atmospheric corrosion; in contact with liquids the electrochemical differences assert themselves more strongly.

It is possible that even annealed metals of high purity may be minutely heterogeneous. Several observers † have recently described the disintegration of lead in contact with an electrolyte. A specimen of sheet lead, immersed in a slightly acid solution of lead nitrate or acetate, gradually becomes loosened in texture, and is ultimately converted into a spongy mass of crystals, the metal being obviously dissolved and re-deposited. The writer has repeated this experiment several times, and finds that it is indifferent whether commercial sheet lead or the purest assay foil be taken. Cold-working is here excluded, as lead anneals itself spontaneously at the ordinary temperature. Whether lead be, as Cohen assumes, a mixture of

* W. Spring, *Bull. Acad. roy. Belg.*, 1903, 1066.

† H. Heller, *Zeitsch. physikal. Chem.*, 1915, **89**, 761; E. Cohen and W. D. Helderman, ibid., 733; H. J. M. Creighton, *J. Amer. Chem. Soc.*, 1915, **37**, 2064.

stable and metastable allotropic modifications, of which the latter would tend to dissolve and recrystallize as the former, remains to be proved.

Local cold-working greatly accelerates corrosion. The severely cold-worked condition which prevails around a punched hole in a boiler-plate is always the spot at which corrosion first appears if opportunity offers. The contact of cold-worked and annealed metal in an engineering structure is for this reason undesirable.

Besides the physical condition of the metal, that of the product of corrosion has to be taken into account. When iron rusts, the product is porous and bulky. It affords a ready passage to the corroding liquids or vapours, whilst at the same time, being strongly electro-negative to iron, the ferric oxide furnishes innumerable local couples which accelerate corrosion. On the other hand, the layer of oxide formed on aluminium under normal conditions is extremely tough and coherent, and prevents further corrosion when a certain small thickness has been reached. Where corrosion is more rapid, the coating may be porous. The loose coating of oxide which is formed when aluminium is rubbed with mercury has no coherence. In moist, tropical countries aluminium corrodes more rapidly, and the coating, although apparently continuous, may be minutely porous. Aluminium drinking vessels in hot climates acquire a foul taste, doubtless owing to the absorptive properties of this porous coating of oxide.

With a view to examining changes in the physical condition of the metal and of the corrosion product, as well as the amount of corrosion, the writer has carried out several series of experiments, mainly in collaboration with Mr. S. Whyte, B.Sc., with alloys of copper with zinc and other metals.* Specimens of the size used for microscopical examination are corroded in a salt solution, being made the anode in a cell of 1 or 2 c.c. capacity with a platinum gauze cathode. If necessary, the action is hastened by the application of a small external e.m.f. A temporary containing vessel is built up of plasticine. After a determined time, the contents of the cell are washed out into a beaker for analysis, and the surface of the specimen is examined. In this way a separate analysis of the products (*a*) to (*e*) may be made, the adherent deposits being removed by gentle scraping if necessary. Special colorimetric methods of analysis are used to determine the proportions of dissolved metals, amounting in some cases only to a hundredth of a milligram or less, and in the continuation of the work microchemical methods are being used. The specimen is examined microscopically at each stage of the process. A convenient laboratory apparatus has been devised, by means of which successive experiments may be made rapidly under exactly similar conditions.†

When an annealed α brass, which consists of a homogeneous solid solution, is corroded under these conditions, using a 5 per cent. solution of sodium chloride and an applied e.m.f. of 2 volts, the surface is attacked, zinc being dissolved much more rapidly than copper, so that a surface layer is obtained, consisting mainly of metallic copper mixed with basic salts. When the latter are removed by washing with very dilute hydrochloric acid, copper is left in very perfect octahedral crystals. It is interesting to observe that this dezincification takes place *per saltum*, there being an abrupt change from copper to unaltered brass, without any intermediate zone in which the proportion of zinc is less than that originally present, but greater than in the superficial layer. This is characteristic of the dezincification of brass,

* Desch and Whyte, *J. Inst. Metals*, 1913, **10**, 304 ; Whyte and Desch, ibid., 1914 **11**, 235 ; Whyte, ibid., 1915, **13**, 80 ; Desch and Hyman, ibid., 1915, **14**, 189.

† Desch, *J. Soc. Chem. Ind.*, 1915, **34**, 258 ; Desch and Hyman, loc. cit.

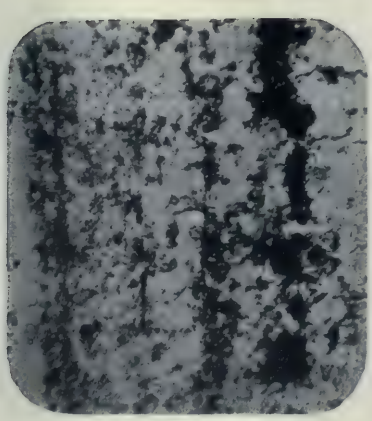


FIG. 1.

Corroded surface of rolled duralumin.
× 50 diam.

FIG. 2.

Transverse section of dezincified brass.
× 250 diam.

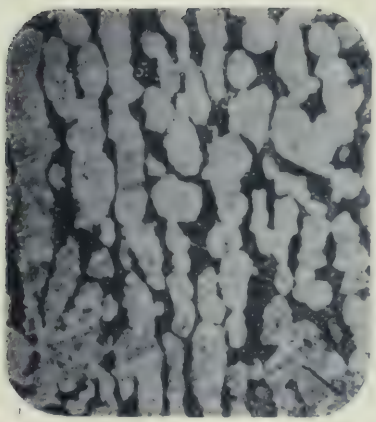


FIG. 3.

Muntz metal in first stage of dezincification.
× 100 diam.

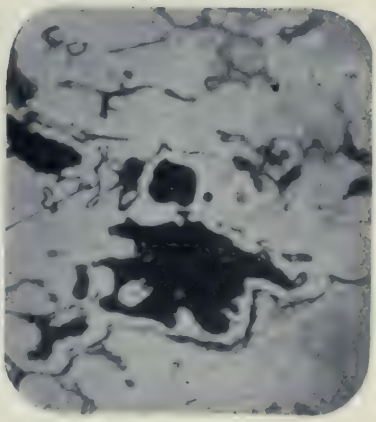


FIG. 4.

Pitting in light aluminium alloy.
× 250 diam.

whether occurring naturally in the course of use or brought about artificially as described above. A transverse section shows this clearly. Under a higher magnification, it is seen that the dezincification proceeds along the boundaries between crystal grains, indicating that the bounding surfaces are more strongly electro-positive than the mass of the crystals. Where twinned crystals are present, as in annealed brass, the removal of zinc also proceeds along twinning planes. Both of these effects are seen in Fig. 2, where the dark, rough areas represent copper invading the brass along boundaries and twinning planes.

The spongy layer of crystalline copper offers a very large surface, and is therefore readily oxidized. This fact accounts for the presence of a bright red layer, consisting mainly of cuprous oxide, on the corroded surface of brass tubes. The oxide layer is of secondary, not primary, origin.

An unannealed cast α brass is not quite homogeneous, but exhibits "coring," each crystal grain becoming richer in zinc from the centre to the periphery. Such an alloy, owing to imperfect homogeneity, is rather more rapidly corroded than annealed brass, but the difference is not large.

The homogeneous β brasses, which are in general too brittle for industrial use, are corroded in a similar manner, but more rapidly. The process is almost entirely one of dezincification, very little copper being dissolved, whilst the residual layer contains sometimes as much as 99·6 per cent. of copper. The crystalline structure of the brass beneath this overlying layer is very clearly developed, and in other respects the process advances just as in the α alloys.

Alloys of the Muntz metal class have a duplex structure, being made up of the α and β solid solutions in conjunction. It was observed by Milton and Larke* that the corrosion of Muntz metal in sea-water proceeds in such a way that a bolt or plate may retain its form and metallic appearance perfectly, although almost devoid of strength. A transverse section shows an outer layer which is copper-red in colour, and often an inner core which is yellow, but brittle and weak, whilst if the corrosion has stopped short of completion there may be a central core of unchanged metal. A similar observation had been made by Arnold,† whose explanation is confirmed by microscopical examination. The β constituent, being the more electro-positive, is first dezincified and converted into a mass of porous, crystalline copper. This stage is seen in Fig. 3, which represents an alloy of this kind after a few minutes' corrosion in the laboratory apparatus described above. The dark β areas are replaced by copper. Only when this change has progressed to some depth does the attack spread to the α crystals, after which the removal of zinc from these proceeds to completion. The spongy copper retains the original form of the crystals, so that a perfect pseudomorph remains, showing the original arrangement under the microscope. This successive replacement of the two constituents by copper was first observed by Arnold,‡ who showed that the strongly electro-positive β was first attacked, and that after its conversion to copper it became electro-negative to α, and so accelerated the corrosion of the latter. When the β has been so far attacked that it has the same composition at the surface as the α, it might seem that a state of equilibrium would be reached, after which the two would be attacked equally, but in fact the great porosity of the partly corroded β causes the attack to be confined to it entirely.

Reversals of electrolytic action of this kind are sometimes very striking. When a mild steel containing manganese is corroded in the small electrolytic

* J. T. Milton and W. J. Larke, *Proc. Inst. Civ. Eng.*, 1903, **154**, 138.
† J. O. Arnold, *Engineer*, 1898, **85**, 363. ‡ Loc. cit.

apparatus, the ferrite only is at first attacked, leaving the pearlite bright and in relief.* The structure at this stage is just the reverse of that produced by etching with acids. Reversal then takes place, and at one point the whole surface is equally darkened, after which the pearlite is more rapidly attacked, and ultimately ferrite is left in relief, as in ordinary etching, The point of reversal coincides with the maximum solution of manganese, and after it is passed the ratio of manganese to iron going into solution again falls.

The effect of a second constituent in accelerating corrosion is also shown in Fig. 4. This represents a light aluminium alloy, containing about 4 per cent. of copper. A eutectic of aluminium and $CuAl_2$ is present, but in such small quantity that a eutectic structure is rarely seen, and the compound mostly presents itself in narrow, isolated masses. When electrolytically corroded in salt solution, the compound remains unattacked, and the ground-mass, instead of dissolving uniformly over its entire surface, is pitted locally, the pits being closely related to the masses of $CuAl_2$, either immediately adjoining them or following their outline at a short distance. The influence of local electrolytic couples is here obvious.

In gun-metals it is the α constituent which is first attacked, the eutectoid δ remaining in relief until the corrosion is very deep. In copper-tin $\alpha\,\beta$ alloys, the electrochemical difference between α and β is very small.

The protective action of certain metals when added to alloys is next to be considered. As the result of experience in the behaviour of alloys in sea-water, the Admiralty introduced the use of 1 per cent. of tin in $\alpha\,\beta$ alloys of copper and zinc. The resulting "naval brass" is much more resistant to corrosion by sea-water than the simpler alloy. The explanation of this effect is not immediately obvious. The 1 per cent. of tin enters into solid solution, and has no effect on the structure beyond slightly increasing the proportion of β, a change in itself conducive to corrosion. The lowering of the electrolytic potential of the brass by the solution of the tin is too small to have any appreciable effect. The experiments cited above have shown that the actual protective effect is in all probability purely mechanical. At first, the presence of tin very slightly accelerates corrosion, but in a neutral or slightly alkaline electrolyte a layer of basic tin salt is rapidly formed, and adheres to the surface so firmly as to form an almost impermeable varnish, which protects the metal from further action. The α brasses are similarly protected by the addition of 1 per cent. of tin, the alloy 70 : 29 : 1 being in common use for condenser tubes.

Lead exerts a protective action on an α brass when present in sufficient quantity. It does not enter into solid solution, and each particle, being electro-negative, causes local dezincification in its immediate neighbourhood. With 1 per cent. of lead, this appears to be the extent of its influence, which is therefore harmful, but a larger proportion of lead gives rise to the formation of a sufficiently tough layer of basic salts. The good quality of condenser tubes containing 2 per cent. of lead is thus explained.

A layer of manganese oxide may exert a protective action. Thus light aluminium alloys, one of which contained 2 per cent. each of copper and manganese, and the other 3 per cent. of copper and 1 per cent. of manganese, became coated with a dark adherent layer when kept for 121 days in sea-water, the corrosion being much less than that of pure aluminium.†

On the other hand, basic salts which fail to form a closely adherent varnish may greatly accelerate corrosion. This is especially so with copper oxy-

* Desch and Whyte, *J. W. of Scotland Iron and Steel Institute*, 1914, **21**, 176.

† W. Rosenhain and F. C. A. H. Lantsberry, Ninth Report to Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1910, 283.

chloride. In a case investigated by the writer, some brass locomotive boiler tubes were found to be very badly pitted, especially at the fire-box end. In each pit was found a small mass of green copper oxychloride, which had served as the electro-negative part of a local couple. The coal used in the locomotive proved to have been repeatedly drenched with sea-water, so that chlorine and hydrogen chloride were formed during its combustion.

The formation of local couples may also be brought about by the adhesion of loose particles of a substance electro-negative to the metal being corroded. It is generally considered that particles of coke often play this part in the corrosion of condenser tubes. This has been disputed in the valuable Second Report to the Corrosion Committee of the Institute of Metals,* but recent experiments † seem to establish it. Such an effect is in accordance with the general behaviour of electro-negative particles.

It is believed that the method of study of corrosion outlined in the present Paper, by taking into account the mechanical and physical factors involved in the process, makes it possible to investigate, with more precision than is possible in the ordinary methods of testing, the mechanism of the process, and it is for this reason that an account of the preliminary results is laid before the Society.

* G. D. Bengough and R. M. Jones, *J. Inst. Metals*, 1913, **10**, 13. For the First Report, see G. D. Bengough, ibid., 1912, **7**, 51.

† A. Philip, ibid., 1914, **12**, 133.

THE RELATIVE CORRODIBILITIES OF IRON AND STEEL.

Dr. J. Newton Friend (Worcester) read a Paper on "The Relative Corrodibilities of Iron and Steel," which had been communicated to the Society by the SHEFFIELD SOCIETY OF APPLIED METALLURGY.

Ever since the discovery of iron man must have been aware of the corrosion of that metal upon exposure to moist air. In the ruins of the ancient Swiss lake villages iron protected by brass or bronze has been found,* showing that the early metallurgists sought to prepare articles combining the strength of iron with the incorrodibility of bronze. In our local museum at Worcester are exhibited bells similar to the Swiss cow-bells, presumably of Roman origin, and which consist of iron coated with brass or bronze. Pliny, writing nearly 2,000 years ago, draws attention to the fact that not only will iron rust, but that some ores yield a metal "which is more particularly liable to rust," thus showing the dawn, even at that early date, of an appreciation of quantitative corrodibility.†

In Pliny's day, and indeed for many centuries later, only a very limited variety of manufactured irons was known, namely, those produced by direct reduction of different ores. At the present time, however, we have to deal with an almost endless series of wrought irons, cast irons, and steels, with the result that the problems of corrosion are each year becoming increasingly numerous and perplexing.

The problem of corrosion is one of the most important that the iron and steel trade has to face. From the economic point of view—and this is a point of peculiar importance at the present crisis—vast possibilities lie in the wake of a correct understanding of the causes leading to corrosion and the best methods of counteracting them. A question which is greatly exercising the minds of both customers and manufacturers is "Which is the more corrodible, iron or steel?" It is with the hope of being able to throw a little light upon this much debated problem that I am venturing to address you to-night.

DIFFERENT KINDS OF CORROSION.

Before dealing directly with the relative corrodibilities of iron and steel, it is desirable to explain exactly what is meant by corrosion. The term is used somewhat widely, but generally speaking may be taken to indicate the solution or oxidation of the pure metal or its constituents. For the sake of convenience three main types of corrosion may be distinguished. These are not to be regarded as isolated and independent; rather are they extreme cases of an almost infinite variety of reactions, dependent upon the composition of the metal and the nature of the corroding influences.

1. *Solution in Acid.*—When immersed in aqueous solutions of many acids,

* Bennett H. Brough, *J. Iron Steel Inst.*, 1906, I, 233.

† See Pliny, Book 34, c. 41.

such as sulphuric or hydrochloric, iron readily dissolves, yielding ferrous salts. If the acid is fairly concentrated* and always present in sufficient excess, the surface of the metal remains relatively bright, and no precipitation of rust takes place. Were it not for the continuous evolution of bubbles of hydrogen gas there would often be little to indicate that the iron is being attacked. If, however, the iron is weighed before and after exposure to the acid the loss in weight occurring may be taken as a measure either of the corrosivity of the liquid or of the corrodibility of the metal.

This is the principle of the so-called acceleration tests, it being assumed that the rate of solution in the acid is a measure of the resistance the metal would offer to corrosion in neutral media—a pernicious supposition contrary to theory and practice alike.† We shall have occasion to refer to this point again in the sequel.

2. *Graphitization.*—This is a form of corrosion to which cast iron is particularly liable, the mass becoming so soft as to be readily cut with a knife. The metallic portion is more or less completely oxidized, mainly to ferrous oxide, some of which has frequently been washed away, the remainder collecting within the pores of the now isolated mass of graphite.‡ This reaction does not usually take place with the purer forms of iron, although a few cases of similar softening are on record where wrought iron has been subjected to prolonged immersion in sea-water.§ The percentage of carbon is, in such cases, of course, much less than with cast iron, but is frequently much higher than the normal in consequence of the solution and removal of some of the iron.

3. *Formation of Rust.*—The most usual form of corrosion is that in which the iron is oxidized more or less completely to brown, hydrated ferric oxide, which remains *in situ* and is popularly known as rust.

When relatively pure iron is suspended in tap-water the ensuing rust consists almost entirely of hydrated ferric oxide, and there is usually no pitting. If, on the other hand, the metal is allowed to become alternately wet and dry, both ferrous and ferric oxides are produced, the proportion of the former varying enormously according to circumstances. In this case pitting is frequent.

When iron is only partially immersed in water, the corrosion just at the surface of the latter is particularly severe and the resulting mass of rust is usually high in ferrous oxide. Complete immersion of iron in concentrated solutions of nitrates of the alkali metals may be made to yield a deep green oxide, whilst a dilute solution of oxalic acid develops a beautiful lemon-yellow form of rust. Dilute phosphate solutions may yield a white rust, whilst alkaline iodides can be made to yield black rust.

Pitting can easily be induced by total immersion in dilute solutions of mineral salts rendered very faintly alkaline by the addition of caustic potash.‖ In such cases the rust invariably contains relatively large quantities of ferrous oxide, in addition to the brown ferric oxide, and the pitting probably occurs at points where slight traces of impurity are present in the metal. Even Kahlbaum's pure iron foil, prepared electrolytically, readily pits in these

* 0·5 per cent. sulphuric acid solution is very suitable.

† See Friend, *The Corrosion of Iron and Steel* (Longmans, 1911), pp. 273–6.

‡ Berzelius, *Traité de Chimie*, 1831, vol. iii. Rennie, *Min. Proc. Inst. Civil Engineers*, 1845, **4**, 323. Draper, *Chem. News*, 1887, **56**, 251. Kröhnke, *Metallurgie*, 1910, **7**, 674. Le Naour, *J. Iron Steel Inst.*, 1898, 1, 526 (abstract). Holgate, *Gas World*, 1913, **58**, 479. Krzizan, *Zeitsch. öffentliche Chemie*, 1912, **18**, 433.

§ Mallet, *British Assoc. Reports*, 1838, p. 259. Lidy, *Engineering News*, 1897, **39**, 85.

‖ Friend, *Science Progress*, 1913, **5**, 202.

circumstances, a fact which proves that certain corroding media are specially liable to induce pitting, since immersion in tap-water or solutions of the majority of inorganic salts merely causes the foil to rust evenly over its entire surface. This fact is one of extreme importance, illustrating the need for investigating the corroding media as well as the metal.

Factors Involved in a Determination of the Relative Corrodibilities of Iron and Steel.

It cannot be too strongly emphasized that the task of satisfactorily determining the relative corrodibilities of iron and steel is one of immense difficulty in view of the numerous factors involved. The five most important of these are as follows :—

1. *The Selection of truly representative Samples of Metal.*—There can be no doubt that many of the incongruities of earlier researches arose from the fact that some investigators worked with poor steel and good wrought iron, thereby obtaining results favourable to the latter ; whilst others examined good steels and poor irons, thus obtaining diametrically opposite results. It must be obvious that the two classes of metal can only be properly compared when thoroughly representative samples of each are dealt with. Since the metals are made in such a variety of ways and with such varying chemical compositions it is essential that a very large number of samples be taken. This is where the majority of the researches are at fault, with the result that the conclusions, although excellent for the field they cover, are not based upon sufficient data to render them of very great practical value.

2. *The Standard of Corrodibility to be adopted.*—Practically all the earlier researches were based upon the loss in weight undergone by the metals when the rust produced by varying corroding media had been removed—a method that is adopted very largely at the present time. In the absence of pitting the results are thoroughly trustworthy and of great value. But, as has been pointed out, certain kinds of corroding media favour the development of serious pitting, and in these cases the mere determination of total superficial loss in weight may not prove particularly helpful. For example, it is conceivable that an iron boiler might lose several pounds in weight through uniform superficial corrosion, and yet not be much the worse. On the other hand, a single ounce removed through pitting might be sufficient to perforate the metal and lead to disastrous consequences. In such cases a determination of the depth of pitting is of the utmost importance, and, as will be seen later, this has been realized by several recent investigators. In the case of bars of iron, Heathcote suggests that determination of the tensile strengths after corrosion would give a measure of the depth of pitting, and this combined with weighing tests should be very valuable.

Another point to bear in mind is that corrosion tests should not in general be carried out to destruction. In practice ironwork usually becomes unsafe long before it is "destroyed" from a corrosion point of view ; and the severity with which corrosion tests are carried out should depend upon the stage at which the metals are to be discarded in practice.

3. *The Corroding Media to be employed.*—No one type of metal must be expected to resist equally well all kinds of corroding media. Some are particularly resistant to acid attack, whilst others withstand the action of fumes easily. Yet a third metal will prove most suitable for resisting neutral corroding agencies, such as river-water or fresh air, whilst a fourth excels in its resistance to the effects of sea-water. These points are strikingly well illustrated by the following data :—

(*a*) Two steels examined by the writer yielded almost identical corrosion factors when exposed to various neutral influences, but in 0·5 per cent. sulphuric acid the second steel corroded 2½ times as rapidly as the first.*

	Corrosion Factors in—				
	Water.	Wet and Dry.	Hot and Cold Water.	Sea Water.	0·5 % H_2SO_4.
Steel 1 ...	100	100	100	100	100
Steel 2 ...	108	100	100	105	259

(*b*) In 1907 Fraser † observed an analogous discrepancy in the behaviour of acid and basic steels of very similar compositions.

	Corrosion Factors of—	
Corroding Medium.	Basic Steel.	Acid Steel.
Air	100	101
River-water	100	101
Rock-salt solution ...	100	90
Common salt solution...	100	106
Sulphuric acid (7·5 %)..	100	306

These, together with the previous results, illustrate very clearly the misleading nature of acceleration tests.

(*c*) Rudeloff,‡ in 1902, found that, by exposing different samples of iron and steel to smelting furnace gases, his wrought-iron plates had the decided advantage, whereas in the tests conducted with air and with ditch-water as corroding media there was much less to choose between the two metals.

From these and numerous other published data it is evident that the nature of the corroding medium must be known before a reliable opinion can be expressed as to the best metal to resist the same.

4. *The Composition of the Metal.*—Steels offer a very wide range for variation of composition, but for present purposes all "special" steels may be eliminated. We are only concerned with those more common types that are used for such purposes as will bear commercial competition with wrought iron. The main chemical differences are thus confined to variations in the carbon and manganese contents. At the present time the influence exerted by these two elements, both singly and together, upon the corrodibility of iron has not been thoroughly investigated. An extensive research on this problem is being carried out by Sir Robert Hadfield and the writer, and although it is too early yet to discuss the results in detail, it may be mentioned that small variations in the manganese content of the metal have

* Friend, Bentley, and West, *J. Iron Steel Inst.*, 1912, I, 249; 1913, I, 388. This variation in acid corroding media was probably due to the fact that steel 2 had a higher manganese content (0·685 per cent.) than steel 1 (0·39 per cent.).

† Fraser, *J. West Scotland Iron Steel Inst.*, 1907, **14**, 82.

‡ Rudeloff. See the tables given later.

been observed to influence, to a hitherto unsuspected extent, the resistance towards corroding media.

Silicon, phosphorus, and sulphur are usually kept fairly low because small increases in their amounts may lead to pronounced alterations in the physical properties of the metal, which would prove awkward in practice. If a given sample of steel happens to possess abnormally high percentages of any or all of these elements, it is either due to accidental circumstances or to meet the special requirements of the customer. In either case the metal falls out of discussion in the present paper.

5. *The Homogeneity and Physical Condition of the Metal.*—Steel is, from the nature of its manufacture, particularly liable to segregation and to variation in its physical condition. It was probably on account of this that the earlier wrought irons frequently had the advantage over the steels. But modern improvements in the manufacture of the two metals have tended to minimize these differences, although the last named have not as yet disappeared and probably never will completely disappear.

Results of Experiment and Experience.

From the foregoing it is evident that our problem is by no means as simple as might appear at the first glance. The factors involved are too numerous to allow of the subject being summarily dismissed in favour either of iron or of steel, as the result of a few isolated laboratory experiments; and whilst theoretical considerations may give us a general idea as to the type of metal that may be expected to withstand corroding media most successfully, there can be no doubt that *the final appeal must always be made to the results of experience and of experiments carried out with a liberal hand on a large scale under actual working conditions.*

More work has been carried out along these lines than the average reader is aware, and the following brief summary of the more important researches may prove useful :—

1. One of the earliest researches carried out on a large scale is that of William Parker,* who, in 1881, exposed plates of seven different kinds of wrought iron and of four varieties of steel to various corroding influences, namely, London air, sea-water, bilge-water, and boiler-water. The results obtained were distinctly in favour of wrought iron, the mean results for the relative losses in weight consequent upon corrosion being—

Wrought iron	100
Steel	133

The results, however, are now of historic interest rather than of practical value, for the simple reason that since 1881 the different processes for the manufacture of both iron and steel have been more or less completely revolutionized.

2. The researches of Rudeloff,† published in 1902, must be placed in a different category, and are worthy of careful consideration. Unfortunately, the analyses of the different metals do not appear to be given, and it is therefore impossible to ascertain to what extent any variation in chemical composition may be responsible for the observed differences in corrodibility. Two sets of experiments were carried out, namely, with plates 0·5 cm. and 0·075 cm. in thickness respectively.

* Parker, *J. Iron Steel Inst.*, 1881, I, 39.

† Rudeloff, *Mitteilungen aus dem königlichen technischen Versuchsanstalten*, Berlin, 1902, **20**, 83. The above tables are compiled and calculated from tables 48 and 49, pp. 176–7 of Rudeloff's memoir.

Metal.	Thickness of Plate.	Dry Air.	Weather.	Smoke.	Ditch Water.	Sea Water.	Mean.
	cm.						
Wrought iron ...	0·5	100	100	100	100	100	100
Wrought iron ...	,,	200	250	0	150	158	
Thomas steel ...	,,	200	207	100	75	193	131
Basic open-hearth steel	,,	200	207	100	175	193	
Wrought iron ...	0·075	100	100	100	100	100	100
Wrought iron ...	,,	146	89	100	84	82	
Thomas steel ...	,,	58	129	200	68	96	106
Basic open-hearth steel	,,	125	79	100	94	113	

Examination of the above tables reveals very considerable differences in the relative corrodibilities of the four metals in different media. The thinner plates exhibit, on the whole, a greater uniformity than the thicker ones; nevertheless, to take the extreme case among the former, the Thomas steel was found to corrode in smoke twice as rapidly as the other metals.

It will also be observed that the thinner steels differed among themselves quite as much as from the corresponding wrought-iron standard.

Finally, it is interesting to note that there was little to choose between the mean corrodibilities of iron and steel in the case of the thinner plates, but the wrought iron had the advantage in the thicker plates.

By exposing the metals to blast furnace gases, however, the wrought-iron plates showed to an overwhelmingly great advantage. The results were as follows :—

	Plates, 0·5 cm. thick.	Plates, 0·075 cm. thick.	Mean.
Wrought iron	100	100	100
Wrought iron	0	67	
Thomas steel	600	183	500
Basic open-hearth steel ...	300	250	

3. Howe and Stoughton * in 1908 gave the results of exposing samples of American iron and steel to various corroding media. They may be tabulated as follows :—

	Weather (2 years).	River Water (2 years).	Sea Water (2 years).	Mean.	Weather (8 years).
Wrought iron	100	100	100	100	100
Steel	103	94	117	105	133

Consideration of the above table shows that there is little difference between the corrodibilities of the iron and steel as exhibited in the tests

* Howe and Stoughton, *Proc. Amer. Soc. Testing Materials*, 1908, **8**, 247.

of 2 years' duration. It is interesting to note, however, that the steel shows to less advantage when the tests are prolonged to 8 years, the corrosion factor for the steel being then 133, which, curiously enough, is the same as the mean value found by Parker (*vide supra*).

The authors point out, however, that mere loss in weight is not the only point to be considered in determining the relative corrodibilities of different metals. Of equal importance is the study of the pitting, because "if there is a hole the water will run out, no matter how much the pipe weighs." Plates of wrought iron and steel were therefore exposed to the action of hot aerated artificial sea-water, and the depths of the pits produced were carefully measured with the following results :—

	Mean Depths of Deepest Pits.	Relative Corrodibilities.
Wrought iron	0·028 inch (mean of 9 plates)	100
Steel	0·017 inch (mean of 12 plates)	61

Here the steel has the distinct advantage, so that from this point of view the relative corrodibilities of the metals are inverted.

Howe and Stoughton also gave the results of an examination of 29 pipes used in the signal systems of an American railroad, 12 of which pipes were steel and 17 iron. Nineteen of these were practically destroyed by corrosion and pitting, the average life of the pipes being as follows :—

	Number of Pipes.	Average Life.	Relative Corrodibilities.
Iron	8	10·4 years	100
Steel	11	13·5 years	77

Here again the steel has the decided advantage.

Ira Woolson in 1910 * reported on 89 samples of pipes from hot-water systems in New York ; 17 of these pipes were of wrought iron, the remainder being steel. No appreciable difference in corrosion was observed.

The succeeding year J. J. Wilson reported on an investigation carried out on the Cresson Coal Field, U.S.A., to the effect that the mean depth of pitting in 20 samples of wrought iron that had seen good service was 0·094 inch, whilst that observed for an equal number of steel samples was 0·093 inch. Here, again, the two metals appeared equally good.

In 1912 W. H. Walker † gave the results of a similar study of iron and steel service pipes, which had been in constant use throughout New England. As the pipes had not been weighed previous to insertion in the water systems, their corrodibilities could obviously not be determined by weighing. The scale and rust were removed and measurements made of the depths of pitting. As the result of 64 comparisons it was found that

Iron corroded more than steel	20 cases
Steel corroded more than iron	18 ,,
Steel and iron equally corroded	9 ,,
Corrosion negligible	17 ,,

* Woolson, *Engineering News*, December, 1910.

† Walker, *J. New England Water Works Assoc.*, 1912, **26**, No. 1.

On the whole therefore there was no difference between the two metals.

The results of several other researches have been published from time to time, but they all bear a similar interpretation.

As a matter of historic interest it may be mentioned that in 1881 the engineers-surveyors of Lloyd's Register possessed no fewer than 1,100 marine steel boilers in actual service, and it was impossible to say which were the more satisfactory, the iron boilers or the steel ones. Even when a boiler of steel was worked alongside of one of iron in the same vessel, no material difference appeared to exist.

Howe * mentioned in 1891 that he communicated with the leading British and American shipbuilders, etc., with a view to finding out their experience as to the relative corrodibility of iron and steel. The opinions received were almost equally divided between the two metals, and may be stated as follows :—

Steel more corrodible than iron	7 firms
Steel less corrodible than iron	8 „
No difference between steel and iron	14 „
Uncertain	8 „

Conclusion.

A study of the preceding data reveals the interesting fact that, whilst the *mean* result of examining a large number of samples of iron and steel after exposure to corroding influences indicates that the two metals are practically equally resistant, yet a very wide divergence exists between the different irons and steels in individual cases.

This is not necessarily due to any irregularity in the metals themselves, as one might be tempted to imagine, but in the majority of cases is attributable to the fact that no one metal can be expected to offer an equal resistance to all types of corroding media.

Our task therefore resolves itself into a wider problem ; not so much as to whether iron is better than steel or *vice versa*, but rather—*Which is the best variety of iron or of steel for any particular purpose?* It is conceivable that certain makes of wrought iron will prove most useful in certain circumstances, whilst under other conditions the palm will have to be given to steel.

* Howe, *The Metallurgy of Steel*, 2nd ed., vol. i., p. 101. New York, 1891.

EXPERIMENTS ON THE INFLUENCE OF COMPOSITION UPON THE CORROSION OF STEEL.

Mr. Leslie Aitchison, M.Met. (Sheffield), read a Paper entitled "Experiments on the Influence of Composition upon the Corrosion of Steel."

Part I.*

For a considerable length of time it has been known that appreciable changes in the rate at which a steel corrodes may be induced by a variation of the composition of the steel. The merely qualitative knowledge that such and such an element causes an increase or a decrease in the rate of corrosion has been superseded, in some measure, by the results of more careful and more systematic observation. Unfortunately, the various workers have each performed their experiments in their own way, and in many cases have obtained results from a series of steels containing any notable quantity of only one element apart from iron and carbon. In consequence it is rather difficult to correlate their results, excellent though each may be.

The present work has been undertaken to supply as far as possible the results of experiments upon steels containing, one at a time, all those elements that enter into the composition of modern steels. The main justification for adding to the already over-large quantity of information upon corrosion is that by performing all the experiments under the same conditions the results obtained upon the various steels may be comparable among themselves.

The corrosion of the steels has been performed in a solution of sodium chloride of approximately the same concentration as that of sea-water. In addition to this, the action of 1 per cent. sulphuric acid upon the steels has been determined, and also their solubility in 10 per cent. sulphuric acid. On the face of it, the operations are not perhaps likely to give much information to those who are endeavouring so earnestly to solve the mystery of the "how and why" of the corrosion of pure iron, but it is claimed that the results should be of value in particular to those whose interest it is to obtain materials with a minimum corrodibility.

The steels used in the experiments are arranged in four different series: (1) Pure iron and carbon; (2) iron with a nearly constant percentage of carbon and a varying proportion of vanadium, tungsten, cobalt, or chromium; (3) iron with a varying percentage of carbon and a nearly constant proportion of manganese, vanadium, tungsten, nickel, or chromium; (4) some steels containing copper. The method of procedure has been as follows. The steels were made in a coke crucible furnace (with the exception of Nos. 19, 20, and 22, which were acid Bessemer steels). The ingots were rolled down to 1-inch bars. From these the requisite length was taken, which was then heated slowly to 900° C. in a gas muffle, maintained at that temperature for half an hour, and then allowed to cool in the air. From these pieces of the bar the corrosion samples were turned—being of the shape and dimensions shown in Fig. 1. The pieces were cleaned with emery paper (down to 00 Fortin), then wiped as free from dust as possible, immersed for half an hour in dry ether, and finally dried in a vacuum desiccator. After that

* Part I of this Paper was communicated to the Society at the Meeting held on May 11, 1915.

they were weighed and suspended in beakers as shown in Fig. 2. In almost every case the weight was within 2 grams of 40 grams, and the area exposed to the action of the solution was from 16 to 19 sq. cm. In each case only pieces containing the same elements were placed in the same beaker. The pieces were then immersed in the various liquids and left, with the beakers covered, for the lengths of time specified. At the end of this period they were taken from the liquid, cleaned with a towel, immersed in dry ether for half an hour, and then, after drying in the vacuum desiccator, weighed again. The pieces were allowed to remain in the sodium chloride and the 1 per cent. sulphuric acid for 77 days in the dark, and in the 10 per cent. acid for 45 hours in the dark. The middle parts of the bar from which the pieces were cut were taken out and prepared for microscopic examination. The final turnings from the pieces were retained for chemical analysis.

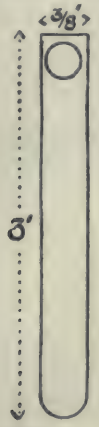


FIG. 1.

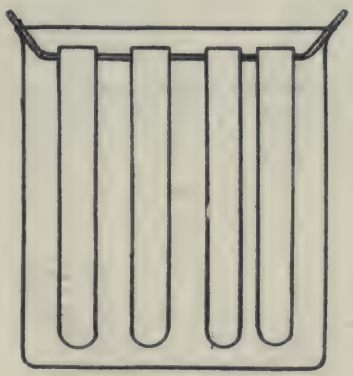


FIG. 2.

In all the tables the results of the corrosion experiments given are the means of duplicates. In general these show a very great concordance, the duplicates agreeing as a rule to about 5 per cent. Any experiment showing serious divergence was repeated.

SERIES I.

TABLE I.

Plain Iron and Carbon Steels—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.
1	0·07	0·018	0·09	0·031	0·010
2	0·19	0·034	0·08	0·030	0·013
3	0·39	0·032	0·09	0·025	0·011
4	0·50	0·051	0·08	0·021	0·015
5	0·76	0·045	0·14	0·025	0·014
6	0·68	0·020	0·15	0·025	0·012
7	1·46	0·046	0·10	0·025	0·012
8	1·05	0·046	0·10	0·023	0·012
9	1·25	0·047	0·14	0·028	0·016
10	0·89	0·049	0·14	0·027	0·014

TABLE II.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4
1	0·07	1·085	2·88	7·02
2	0·19	1·080	3·48	7·15
3	0·39	1·004	4·33	6·63
4	0·50	0·992	3·34	4·57
6	0·68	1·080	4·15	6·90
5	0·76	1·060	—	7·13
10	0·89	1·196	4·25	10·82
8	1·05	1·196	—	7·33
9	1·25	1·178	4·38	6·65
7	1·46	1·132	3·57	4·90

(Cf. Figs. 11 and 12.)

The microstructures of these steels are perfectly normal and show nothing at all out of the ordinary. In each case the pearlite is that mixture of much

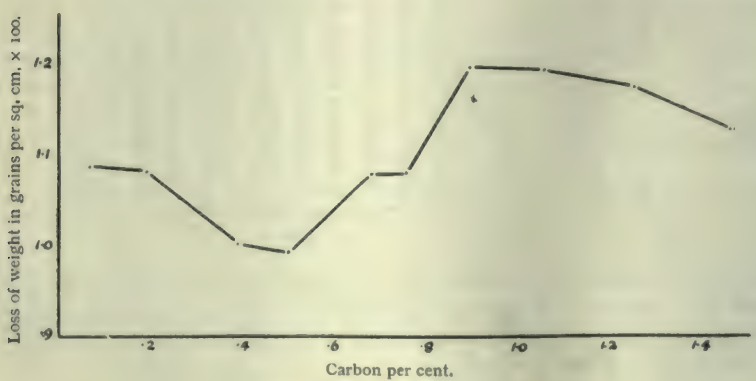


FIG. 11.—3 per cent. NaCl.

laminated and little sorbitic which is so characteristic of plain carbon steel cooled in air in the manner employed here. Those containing more than 1 per cent. of carbon had the cementite as thin plates, not as nodules. It may be seen from Table II that, contrary to the usually accepted idea, the corrosion in 3 per cent. sodium chloride does not show a continuous increase from the lowest carbon to 0·9 per cent., but actually shows a decrease during the increase of carbon to about 0·45 per cent. After that there is an increase to a definite maximum at 0·9 per cent., when a further addition of carbon causes a falling off. These variations in the corrosion are reproduced almost exactly by the 10 per cent. sulphuric acid, the maximum at 0·9 per cent. being very marked (Heyn and Bauer * obtained a curve of similar shape, but in their case the maximum came at 0·45 per cent.). The results with the 1 per cent. acid are not quite like those with the 10 per cent., but do not contradict them except in the fact that here the minimum corrosion is obtained with the purest material. (Chappell † has given a curve

* *Journal of Iron and Steel Inst.*, 1909, ii. 186.
† Ibid., 1912, i. 270.

for a smaller but fairly similar series of steels. He also obtains a maximum at 0·9 per cent. carbon, but has no evidence of a minimum at a lower percentage.) It will be noted that in the case of the sodium chloride solution there is not a very great difference (about 20 per cent.) between the most corrodible steel and the least.

SERIES II.

TABLE III.

Steels containing Tungsten—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	W %.
43	0·68	0·061	0·15	0·025	0·017	26·3
44	0·73	0·063	0·15	0·024	0·016	21·5
45	0·70	0·037	0·13	0·021	0·014	9·74
46	0·72	0·107	0·16	0·023	0·015	5·37
47	0·74	0·032	0·14	0·026	0·014	14·96
48	0·74	0·107	0·15	0·025	0·016	2·36

TABLE IV.

Loss of Weight per sq. cm. × 100.

No. of Steel.	W %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
48	2·36	1·54	6·50	8·42
46	5·37	2·01	7·27	7·85
45	9·74	1·72	4·13	9·10
47	14·96	1·75	6·65	4·13
44	21·5	2·18	6·77	11·8
43	26·3	1·97	4·11	8·05

TABLE V.

Steels containing Chromium—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	Cr %.
23	0·84	0·06	0·10	0·019	0·02	0·99
24	0·85	0·11	0·09	0·020	0·022	10·15
25	0·84	0·08	0·11	0·021	0·021	4·97
26	0·88	0·03	0·12	0·020	0·018	15·02
27	0·85	0·11	0·09	0·018	0·019	19·46
28	0·85	0·20	0·10	0·022	0·020	23·70

TABLE VI.

Loss of Weight per sq. cm. × 100.

No. of Steel.	Cr %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
23	0·99	1·31	12·6	15·9
25	4·97	1·38	5·4	11·0
24	10·15	0·79	10·3	18·3
26	15·02	0·91	5·85	33·6
27	19·46	0 00	0·52	29·0
28	23·70	0·24	1·76	23·7

(Cf. Fig. 13.)

TABLE VII.

Steels containing Cobalt—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	Co %.
63	0·73	0·05	0·16	Less than 0·04	Less than 0·02	2·68
64	0·65	0·07	0·18			5·50
65	0·75	0·10	0·23			16·97
66	0·72	0·11	0·25			20·85
67	0·75	0·09	0·23			11·18

(Cf. Fig. 14.)

TABLE VIII.

Loss of Weight per sq. cm. × 100.

No. of Steel.	Co %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
63	2·68	1·55	8·73	5·12
64	5·50	1·31	6·38	3·50
67	11·18	1·26	5·82	2·28
65	16·97	1·17	3·13	1·13
66	20·85	1·25	2·80	1·03

TABLE IX.

Steels containing Vanadium—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	V %.
33	0·60	0·05	0·06	0·041	0·010	0·71
34	0·63	0·09	0·07	0·042	0·011	2·32
35	0·93	0·21	0·11	0·039	0·018	5·84
36	1·07	0·32	0·12	0·041	0·030	10·30
37	1·10	0·47	0·12	0·040	0·031	13·45

TABLE X.

Loss of Weight per sq. cm. × 100.

No. of Steel.	V %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
33	0·71	1·73	5·82	8·05
34	2·32	1·74	4·73	12·42
35	5·84	1·87	4·48	22·25
36	10·30	1·66	5·56	17·40
37	13·45	1·49	3·63	16·18

It will be seen in this series that in the case of the corrosion in sodium chloride the presence of the added element causes, at first, an increase in the corrosion of the material in every group over that sustained by the pure iron carbon steel containing the same percentage of carbon. This is reflected

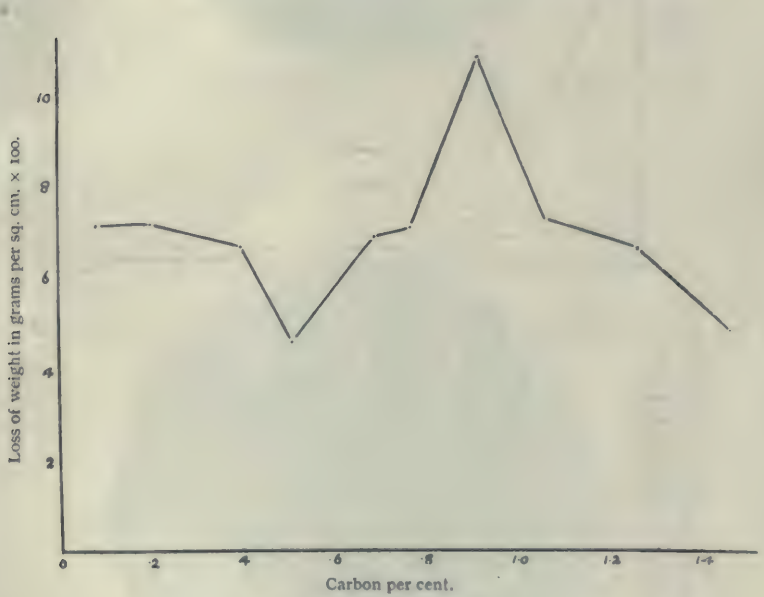


FIG. 12.—10 per cent. H_2SO_4.

in the microstructure, which shows, in each case, that the introduction of the third element produces a pearlite which is in a much finer state of division than that of the plain carbon steel. In general, too, the size of the grain has been altered—usually being decreased.

In the tungsten group it is obvious that the general trend of the corrosion in all the three media is the same. The sodium chloride and 10 per cent. acid each shows a maximum at 21 per cent. of tungsten, followed by a fall when the tungsten rises to 26 per cent. The 1 per cent. acid also shows this fall. The microstructure of the 21 per cent. steel (Fig. 3) shows that the

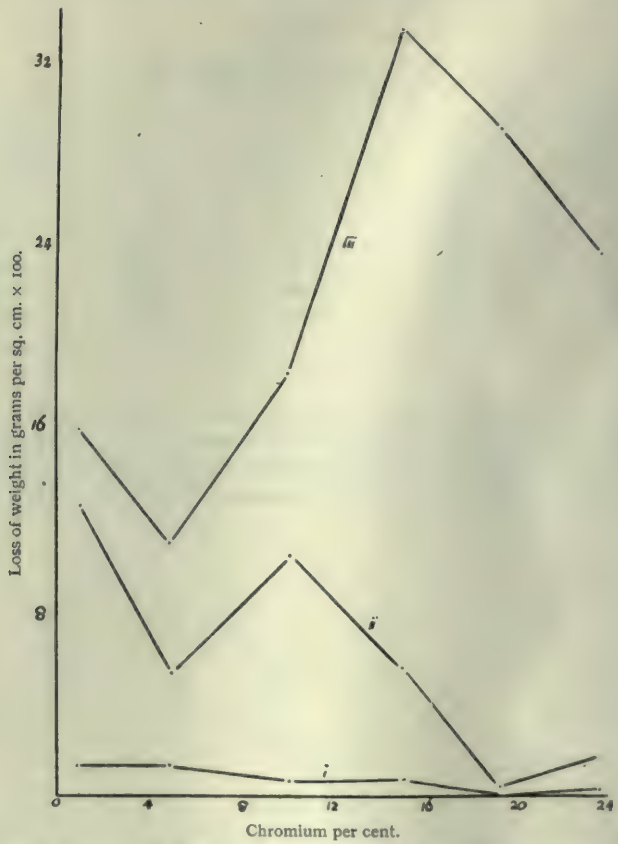


FIG. 13.—i. 3 per cent. NaCl. ii. 1 per cent. H_2SO_4. iii. 10 per cent. H_2SO_4.

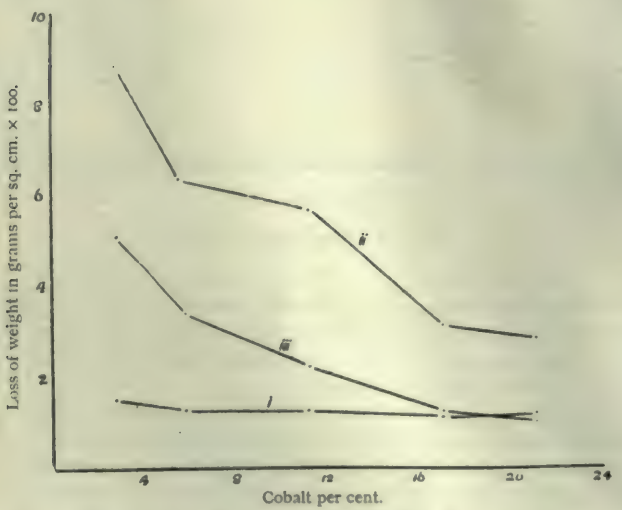


FIG. 14.—i. 3 per cent. NaCl. ii. 1 per cent. H_2SO_4. iii. 10 per cent. H_2SO_4.

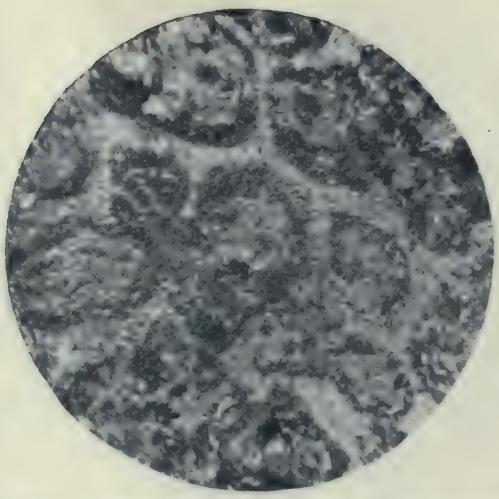


FIG. 3.—Steel containing 21 per cent. Tungsten (× 500).

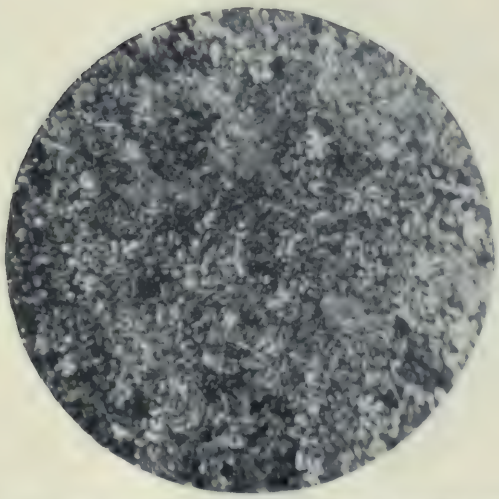


FIG. 4.—Steel containing 26 per cent. Tungsten (× 500).

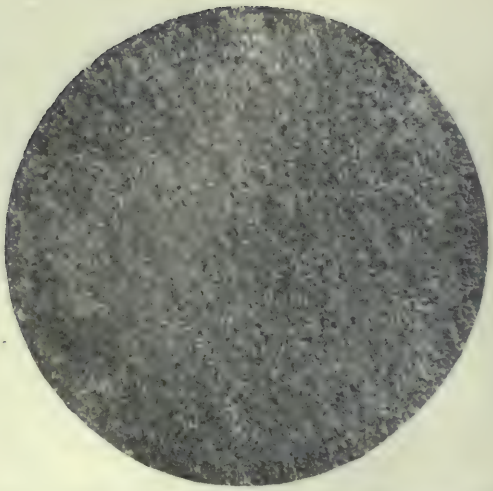


FIG. 5.—Steel containing 6 per cent. Vanadium (× 100).

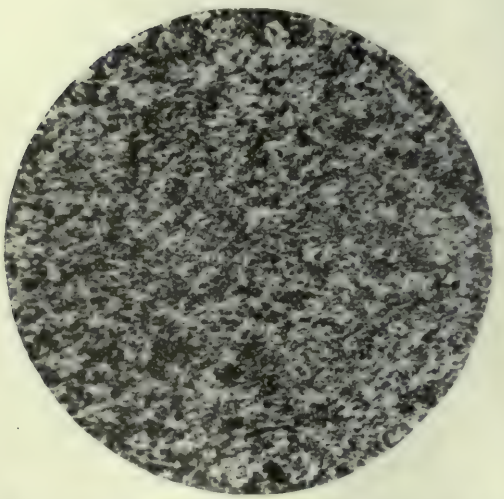


FIG. 6.—Steel containing 13·5 per cent. Vanadium (× 100).

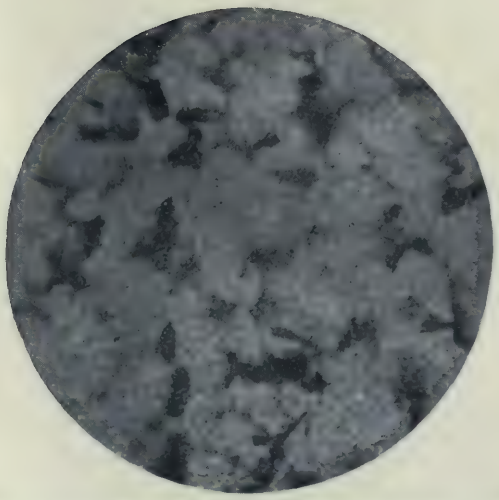


FIG. 7.—Steel containing 6 per cent. Chromium (× 500).

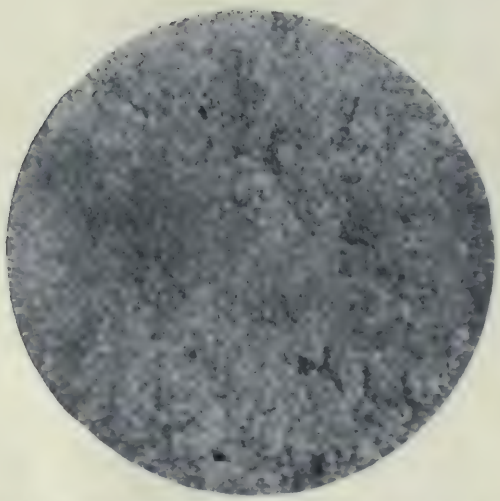


FIG. 8.—Steel containing 19 per cent. Chromium (× 500).

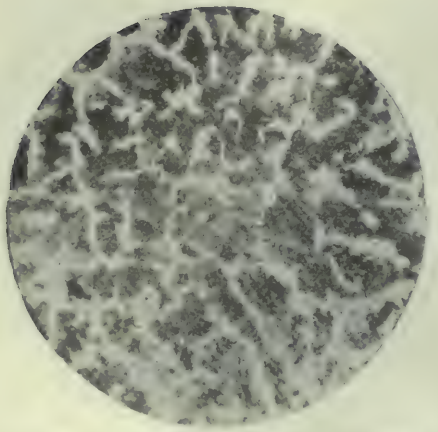


FIG. 9.—Steel containing 5·5 per cent. Cobalt (× 150).

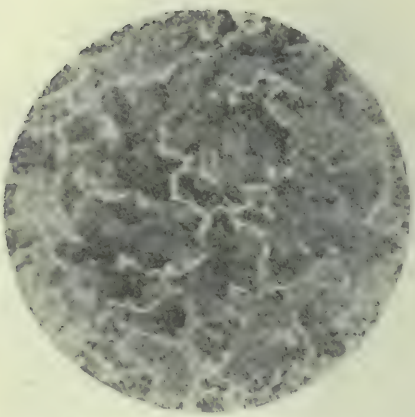


FIG. 10.—Steel containing 17 per cent. Cobalt (× 150).

quantity of excess carbide rises to its maximum (Arnold and Read*) in this steel, and that the 26 per cent. steel has less of this excess constituent (Fig. 4).

The vanadium steels in all three solutions show that one particular composition presents a maximum corrodibility. In the case of the sodium chloride and the 10 per cent. acid, this occurs at about 10 per cent. of vanadium, whilst in the 1 per cent. acid at about 6 per cent. In general, these vanadium steels rank among the most readily corrodible. The microstructures show considerable changes. Starting with the low vanadium steels, which have pearlite and ferrite, increase of vanadium produces a microstructure which is marked by a background of conspicuously fine structure (Fig. 5), overlaid with white meshes. This in general produces an increase of corrosion. Going further with the addition of vanadium, the background becomes apparently structureless, but the quantity of white carbide increases a great deal (Fig. 6). This has brought with it a decrease of the corrosion (cf. the chromium steels, *infra*).

The steels containing chromium are very interesting. Here again the first influence of the added element is to cause an increase in the corrosion. Then in the milder corrosion of the sodium chloride and the 1 per cent. acid a remarkable fall occurs. In the case of the 19·5 per cent. chromium steel absolutely no corrosion took place in the sodium chloride and practically none in the 1 per cent. sulphuric acid. This fall in the corrodibility commenced at 10 per cent., this composition being marked also by the first appearance of any quantity of white carbide (Arnold and Read†). As the quantity of this carbide increases, there is a fall in the corrodibility, later followed by a slight increase of corrosion in the steel of highest chromium content. Curiously enough, the same constituent causes a violent increase in the solubility of the steels in the strong acid, a solubility which has been falling off prior to this. The microstructures of the 6 and 19 per cent. steels are appended (Figs. 7 and 8). This decrease of corrosion with an increase of chromium has been shown also by Friend, Bentley, and West,‡ Hadfield,§ and Monnartz.‖

The cobalt steels show no peculiarities except the fall of corrosion, which is quite uniform in all the steels practically to the end of the series. In the one containing most cobalt this is probably helped in a measure by the fact that the steel contained a small proportion of graphite. As a result of this, in some areas there is a good deal of ferrite, and but little pearlite. In consequence there is less surface at which galvanic action can take place. The microstructures of these steels do not show anything out of the ordinary (Figs. 9 and 10). (Burgess and Aston,¶ have shown that the introduction of cobalt into pure iron lowers the tendency to corrode, though not to the same extent as occurs with nickel.)

* *Journal Inst. Mech. Eng.*, 1914, 239.
† *Journ. Iron and Steel Inst.*, 1911, i. 249.
‡ Ibid., 1912, i. 249.
§ Ibid., 1892, ii. 92.
‖ *Metallurgie*, 1911, viii. 161.
¶ *Eighth Int. Cong. Applied Chemistry*, 26, 479.

SERIES III.

TABLE XI.

Steels containing Tungsten—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	W %.
49	0·47	0·061	0·08	0·051	0·011	3·09
50	0·20	0·048	0·08	0·048	0·012	3·22
51	0·58	0·08	0·09	0·052	0·011	3·16
52	0·88	0·04	0·10	0·041	0·010	3·07
53	1·08	0·038	0·08	0·041	0·012	3·11

TABLE XII.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
50	·20	1·56	2·16	2·80
49	·47	1·68	2·87	5·37
51	·58	1·83	6·4	4·95
52	·88	1·04	3·69	5·13
53	1·08	1·70	3·98	4·83

TABLE XIII.

Steels containing Vanadium—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	V %.
38	0·11	0·034	0·19	0·018	0·020	0·17
39	0·38	0·038	0·28	0·020	0·022	0·22
40	0·73	0·036	0·33	0·019	0·021	0·21
41	0·96	0·04	0·36	0·016	0·020	0·20
42	1·30	0·035	0·31	0·019	0·021	0·21

TABLE XIV.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
38	·11	1·89	4·32	14·41
39	·38	—	5·22	13·83
40	·73	1·92	2·88	9·05
41	·96	2·48	3·73	9·25
42	1·30	2·57	4·28	7·78

TABLE XV.

Steels containing Chromium—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	Cr %.
29	0·33	0·048	0·22	0·025	0·012	1·97
30	0·52	0·050	0·21	0·027	0·011	2·01
31	0·64	0·046	0·24	0·026	0·012	2·05

TABLE XVI.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
29	·33	1·31	1·74	17·1
30	·52	1·17	—	10·7
31	·64	1·46	2·3	11·1

TABLE XVII.

Steels containing Nickel—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	Ni %.
54	0·07	0·043	0·13	0·013	0·014	3·07
55	0·28	0·049	0·14	0·014	0·016	3·13
56	0·48	0·046	0·14	0·012	0·015	2·94
57	0·88	0·042	0·18	0·011	0·016	2·97
58	0·76	0·05	0·19	0·012	0·015	3·08

TABLE XVIII.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
54	·07	1·39	1·59	4·12
55	·28	1·57	1·28	4·09
56	·48	1·87	1·88	5·42
58	·76	1·91	6·48	10·13
57	·88	1·52	12·3	4·83

TABLE XIX.

Steels containing Manganese—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.
19	0·28	0·03	0·94	0·042	0·037
20	0·48	0·028	0·91	0·043	0·038
22	0·87	0·035	1·01	0·039	0·034
11	0·76	0·078	0·83	0·041	0·019

TABLE XX.

Loss of Weight per sq. cm. × 100.

No. of Steel.	C %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
19	·28	1·82	8·16	8·05
20	·48	1·94	9·70	8·80
11	·76	2·50	4·67	12·3
22	·87	1·88	7·08	6·12

The tungsten steels in Series III show an increase of corrosion in the sodium chloride for the first part of the group and then a drop from the saturation-point. In all three corrosion media there is a sharp rise up to 0·6 per cent. of carbon—just the reverse of the plain carbon steels.

The presence of even so little as 0·2 per cent. of vanadium has increased the corrodibility of the steels to a great extent, though the solubility in the 10 per cent. shows a decrease and not an increase with a rise of carbon.

The presence of only 3 per cent. of nickel has not been sufficient to cause the fall of corrosion noticed by many workers with a higher percentage of this element (Howe* and Diegel †). In fact, an increase of corrosion is found, particularly in the higher members. It is to be noticed that in the lower members of this series the pearlite has resolved itself in a great degree into ferrite and cementite, there being little ordinary pearlite. In the higher members, however, it has assumed an appearance more like that of ordinary plain carbon steels. This change of structure, however, would not appear to account for the rise of corrodibility from the start.

Manganese has the general effect of lowering the saturation-point of a steel as well as of producing sorbitic pearlite. This agrees quite well with the corrosion results, the maximum occurring at the saturation-point of the steel (a little below 0·8 per cent. carbon). With the 1 per cent. acid the curve is inconclusive, but the 10 per cent. shows also a maximum near the saturation-point.

The presence of only 2 per cent. of chromium has caused an increase of the corrosion. This is not surprising in view of the change produced in the microstructure of the pearlite by the introduction of the chromium. In all

* *Journ. Iron and Steel Inst.*, 1900, ii. 567.

† *Verhandlungen des Vereins zur Beforderung des Gewerbfleisses*, 1903, 5, 157.

cases the coarseness and laminations of the pearlite in the plain carbon steels, have been replaced by a finely divided sorbitic pearlite.

SERIES IV.

TABLE XXI.

Steels containing Copper—Chemical Analysis.

No. of Steel.	C %.	Si %.	Mn %.	S %.	P %.	Cu %.
59	1·18	0·06	0·20	0·021	0·043	0·48
60	0·59	0·063	0·16	0·02	0·049	1·06
61	0·38	0·066	0·18	0·026	0·018	2·52
62	0·3	0·062	0·28	0·038	0·016	4·78

TABLE XXII.

Loss of Weight per sq. cm. × 100.

No. of Steel.	Cu %.	3 % NaCl.	1 % H_2SO_4.	10 % H_2SO_4.
59	0·48	1·86	15·1	58·3
60	1·06	2·13	6·58	0·69
61	2·52	2·31	9·45	0·92
62	4·78	2·07	3·22	1·02

The question of the corrosion of steels containing copper is one still very much under debate. The present figures show that corrosion in sodium chloride is considerably increased by the presence of the copper, and that in the 1 per cent. acid there is a general increase. In the strong acid there is, however, a distinct decrease of the corrosion, with the exception of the steel containing but half a per cent. of copper. Those containing more copper show very little attack. This is in a measure, no doubt, due to the fact that the whole ferritic surface of the material becomes covered with a layer of copper. This is almost certainly produced during the early parts of the attack, when copper is taken into solution, and from which it is afterwards precipitated in the usual way by the iron, on to the surface of the ferrite. This film is quite apparent and appears to act powerfully as a deterrent, as might be expected from the normal action of copper on sulphuric acid.

It is hoped that further matter relative to the corrosion of these steels may be brought forward in the near future. Any conclusions to be drawn from the above experiments will not be put forward till this additional evidence has appeared.

My best thanks must be given to Professor J. O. Arnold, D.Met., F.R.S., for his generosity in allowing me to make use of the many steels prepared for his own researches.

METALLURGICAL DEPARTMENT,
SHEFFIELD UNIVERSITY.

EXPERIMENTS ON THE INFLUENCE OF COMPOSITION UPON THE CORROSION OF STEEL.

Part II.

The following results show the effect of ordinary tap-water upon the same steels whose corrosion in 3 per cent. sodium chloride solution, in 1 per cent. and 10 per cent. sulphuric acid has been presented already. The results in water correspond more to the ordinary "rusting" which occurs so regularly in everyday experience. The method of preparation of the steels was exactly the same as in the previous experiments, and in this case the pieces were suspended in tap-water in glass beakers in the dark. They were immersed during 77 days, but in this case the water was renewed seven times (at regular intervals) during the progress of the corrosion, the rust adhering to the pieces being shaken off gently before the pieces were put into the fresh water. The pieces after corrosion were cleaned and dried in the usual manner. As before, the results given of loss of weight are the mean of concordant duplicate experiments, and in the tables the loss of weight in grams per square centimetre is multiplied by a hundred.

Series I.*

Pure Iron and Carbon Steels.

No. of Steel.	C %.	Loss of Weight per cm.^{2} × 100.
1	0·07	0·875
2	0·19	0·860
3	0·39	0·866
4	0·50	0·88
6	0·68	0·89
10	0·89	0·92
8	1·05	0·92
9	1·25	1·02
7	1·46	1·01

The steels do not display the same regularity in their corrosion in tap-water that they did in the 3 per cent. sodium chloride solution or in the 10 per cent. sulphuric acid. So far as they may be compared with any of the results obtained previously, they appear to show a greater similarity to

* The complete analyses of all the steels used in all the experiments were given in Part I, *q.v.*

the effects produced in 1 per cent. sulphuric acid than any other. There is, however, again the fall of corrosion at first with the rising carbon from bar iron to steel with 0·4 per cent. of carbon noticed in the case of brine and the 10 per cent. sulphuric acid. (This is referred to again in Part III, *infra.*) After this original fall there is a regular, gradual rise of the corrosion from 0·4 per cent. to 1·46 per cent. of carbon (cf. Fig. 1). Comparing with the corrosion in brine it may be seen that the actual loss of weight is almost as great in the tap-water as in the 3 per cent. sodium chloride solution, the minimum ratio being 0·77 for the steel containing 0·89 per cent. carbon, and the maximum being 0·89 in the 1·46 per cent. carbon steel.

In Series II there are several prominent irregularities, though many interesting results emerge. In the tungsten steels the addition of the third element has increased the corrosion throughout the series. (For the corresponding pure carbon series the loss in grams per square centimetre × 100 is

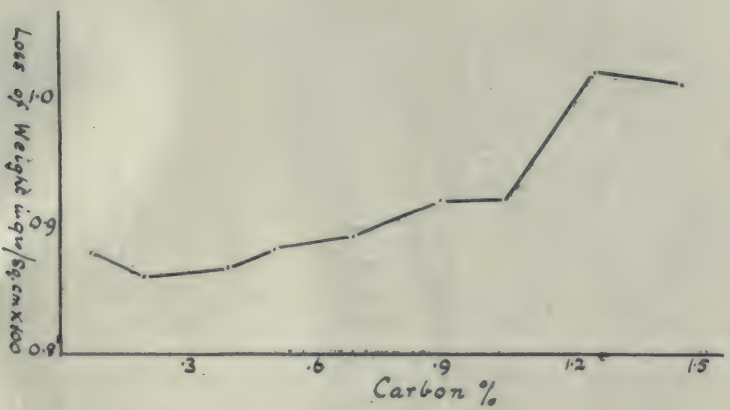


FIG. 1.

0·9.) The increase of corrosion over that experienced by the pure carbon steels is not so great in any part of the series as was the case with the attack by sodium chloride solution. The definite maximum at 15 per cent. tungsten is quite unique to the water corrosion. The microstructure of this steel shows that it has very thin walls of a carbide * overlying the solid solution. This is the first steel in the series which shows this carbide quite free. (It may be seen from Arnold and Read's paper that the "saturation" point of the tungsten series occurs at about 11·5 per cent. tungsten and 0·72 per cent. carbon, and that consequently any excess of tungsten over this may possibly appear as structurally free carbide.) It might be expected in consequence of this change of microstructure that some difference in the corrosion would be introduced by the new constituent. (This point, and possible conditions of difference between the action in water and in sodium chloride solution or sulphuric acid, are discussed in Part III, *infra.*) Although the proportion of this excess carbide rises higher in the next steel (the one containing 21·5 per cent.), the form of it changes to a considerable extent. From being of the nature of cell walls it becomes more granular, and does not surround the crystals to the same extent.

* Cf. Arnold and Read, *Journ. Inst. Mech. Eng.*, 1914, 239.

SERIES II.

Tungsten Steels.

No. of Steel.	C %.	W %.	Loss of Weight per cm.² × 100.
48	0·74	2·36	0·970
46	0·72	5·37	0·930
45	0·70	9·74	0·976
47	0·74	14·96	1·100
44	0·73	21·5	0·940
43	0·68	26·3	0·970

Cobalt Steels.

No. of Steel.	C %.	Co %.	Loss of Weight, per cm.² × 100.
63	0·73	2·68	0·94
64	0·65	5·50	0·95
67	0·75	11·18	1·06
65	0·75	16·95	0·74
66	0·72	20·85	1·12

Chromium Steels.

No. of Steel.	C %.	Cr %.	Loss of Weight per cm.² × 100.
23	0·84	0·99	0·845
25	0·84	4·97	0·652
24	0·85	10·15	0·452
26	0·88	15·02	0·453
27	0·85	19·46	0·154
28	0·85	23·70	0·000

Vanadium Steels.

No. of Steel.	C %.	V %.	Loss of Weight per cm.² × 100.
33	0·60	0·71	0·90
34	0·63	2·32	0·85
35	0·93	5·84	0·86
36	1·07	10·3	0·79
37	1·10	12·45	0·85

The cobalt steels give results differing very much from those obtained previously. In place of the very regular fall of corrodibility throughout the series, noticed with these other media, the attack by water is distinctly irregular. Still more peculiar is the maximum attack with the steel containing the largest percentage of cobalt. This following upon the minimum of corrosion with the next highest steel in the series is difficult of explanation. With the exception of this latter steel it will be noticed that the addition of the cobalt has caused an increase in the corrosion over that of the pure carbon steel, though once again not to the same extent as in the attack by the brine.

The chromium series presents one feature of particular interest. In the corrosion by sodium chloride solution, and 1 per cent. sulphuric acid, the steel containing 19·46 per cent. of chromium was quite or almost unattacked by the medium, whilst the one with 23·7 per cent. chromium was attacked rather more. In this case—the corrosion by water—the steel with the highest proportion of chromium does not corrode at all, whilst the one that was unattacked by the sodium chloride solution is now corroded to a slight extent. With increasing chromium the corrosion falls throughout the series, the steel containing the largest proportion of free carbide being the least attacked. In this corrosion medium there is no increased attack with the lower percentages of chromium over that sustained by the corresponding pure carbon steel, as was the case in the brine.

The addition of the vanadium has produced a relatively small variation in the corrodibility of the steel, though curiously enough it has made the corrosion by water less than for the pure carbon steels, whilst in the case of the sodium chloride solution the presence of the vanadium caused an increased loss. In the sodium chloride solution and in 1 per cent. sulphuric acid there was noticed a general tendency to a decrease of corrosion with an increase of vanadium. This is supported by the action—in this case—of the water.

In Series III, in the tungsten set there is shown the interesting fact that the addition of 3 per cent. of tungsten has produced a decrease of the corrosion. This was noticed also in the attack by both 1 and 10 per cent. sulphuric acid, but was not found in the case of the sodium chloride solution —where an increased corrosion was experienced. In this series with water there is quite a regular fall to a minimum followed by a rise, to be noticed.

The vanadium steels, though irregular, may be taken to show that the addition of this small percentage of vanadium has had practically no effect upon the corrodibility. This is not at all the result obtained with the other three corrosion media in which a distinct increase of the corrosion was obtained, as a whole. The 2 per cent. chromium steels in this case—unlike the results obtained with sodium chloride and sulphuric acid—show a slight though firm decrease at all three percentages of carbon.

The nickel steels give apparently regular results and show themselves largely in conformity with the attack by sodium chloride and by the 10 per cent. sulphuric acid. In these three cases—water, brine, and 10 per cent. acid—there is a distinct rise of corrosion with increase of carbon at the start, followed by a fall to the material with the highest proportion of carbon. At the two ends of the series (in water) the corrodibility has been decreased by the presence of 3 per cent. of nickel, whilst in the middle (from 0·3 to 0·8 per cent. carbon) it has been increased. The manganese steels are quite irregular in their behaviour, though it appears fairly certain that the addition of manganese causes an increased corrodibility in water, as well as in the other media.

SERIES III.

Tungsten Steels.

No. of Steel.	C %.	W %.	Loss of Weight per cm.² × 100.
50	0·20	3·09	0·793
49	0·47	3·22	0·759
51	0·58	3·16	0·642
52	0·88	3·07	0·742
53	1·08	3·11	0·800

Vanadium Steels.

No. of Steel.	C %.	V %.	Loss of Weight per cm.² × 100.
38	0·11	0·17	0·900
39	0·38	0·22	0·820
40	0·73	0·21	0·995
41	0·96	0·22	0·932
42	1·3	0·21	1·035

Chromium Steels.

No. of Steel.	C %.	Cr %.	Loss of Weight per cm.² × 100.
29	0·33	1·97	0·800
30	0·52	2·01	0·825
31	0·64	2·05	0·812

Nickel Steels.

No. of Steel.	C %.	Ni %.	Loss of Weight per cm.² × 100.
54	0·07	3·07	0·802
55	0·28	3·13	0·870
56	0·48	2·94	1·086
58	0·76	3·08	0·966
57	0·88	2·97	0·895

Manganese Steels.

No. of Steel.	C %.	Mn %.	Loss of Weight per cm.² × 100.
19	0·28	0·94	0·900
20	0·48	0·91	0·960
11	0·76	0·83	0·872
22	0·87	1·01	1·43

SERIES IV.

Copper Steels.

No. of Steel.	C %.	Cu %.	Loss of weight per cm.^{2} × 100.
59	1·18	0·48	1·03
60	0·59	1·06	0·820
61	0·38	2·52	0·980
62	0·30	4·78	1·10

The results obtained with the copper steels are faintly reminiscent of the attack by 10 per cent. sulphuric acid. In general, too, there is an increased corrosion over that sustained by the pure carbon steels—as was the result with sodium chloride solution.

The tap-water employed in the foregoing experiments gave the following mean analysis :—

	Grains per Gallon.
Total solids	7·30
SiO_2	0·56
Fe_2O_3 and Al_2O_3	0·21
$CaCO_3$	1·04
Chlorine	0·89
H_2SO_4	1·70
MgO...	0·51
Alkaline salts : H_2O in combination, etc. ...	2·39

Oxygen consumed, 2·4 parts per million of water.

PART III.

MICROSCOPIC EVIDENCE OF THE INFLUENCE OF COMPOSITION ON THE CORROSION OF THE STEELS.

After the chemical analysis of a steel, nothing is of greater importance than its microstructure. The various changes in composition of steels are reflected completely in the microstructure, and not only the composition, but also the heat treatment. In the series of steels under consideration, no attempt has been made to vary the heat treatment—in all cases they have been normalized at 900° C., but this does not mean that they are all in the same condition with reference to heat treatment. The various thermal equilibrium diagrams of the different systems of ternary alloys necessitate that this slow heating to 900° C., followed by a normal cooling, should produce different types of structure in the different steels (quite apart from chemical composition as such), depending upon the position of the change points, etc. This, of course, is no disadvantage for the purpose in hand, since the different types of structure that are produced have each their quota of information to provide.

It is almost a platitude to say that from the chemical composition of a steel alone, it is impossible to forecast the resulting microstructure, and certainly from the microstructure nothing but an extremely wide experience and a good guess will enable an observer to estimate the chemical composition. Certainly, the actual structures of steels of one type are fairly uniform, e.g. the high tungsten series show a regular change, each of which might

have been foretold had the structure of the steels above and below been known. But to distinguish between a high tungsten and a high chromium steel simply by the microstructure would be next to impossible—both being in the region productive of solid solution and excess carbide. Yet these two structures, so singularly alike, give entirely different results when corroded.

Structural Details to be Considered.—Amongst the points to be considered, the actual constituents present in the steels of the series are of primary importance. In the series of steels involved in these experiments the majority of the constituents found in steels are to be met with. The plain carbon steels have of course ferrite, cementite, and pearlite. The latter constituent is found in various of the forms in which it is generally encountered—passing from the ordinary, rather jumbled pearlite of a normal steel and which is found uniformly throughout the plain carbon steels, to sorbitic pearlite (which is found usually in manganese steels) on the one hand, and to the almost entirely segregated ferrite and cementite on the other. This latter variety is found in the nickel steels containing the lower percentage of carbon. It might be inferred quite naturally that such diverse structures would produce quite different results under the influence of the corrosion media.

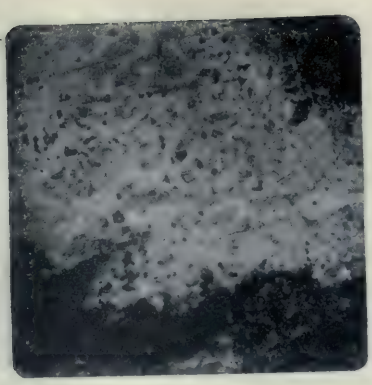
Pearlite is also found in a large number of the other steels—broadly in all those with less than 4 per cent. of the third constituent. In these steels the pearlite is usually of the small variety, the cementite being in small globules dotted about the ferrite, rather than the laminæ more generally observed. As the carbon or the percentages of the third element increases, the excess of carbide shows itself in a quite free form. This is, in general, accompanied by the substitution of solid solution for pearlite in the structure.

These carbides (an account of which may be found in the various papers of Arnold and Read *) are of widely different compositions, but of considerable similarity of properties. Usually they appear in one of three forms—as part of the pearlite, as boundaries to the grains of solid solution, or as globules dotted about throughout the solid solution with apparently no relationship to the boundaries of the grains. In all cases they are found as pure white constituents after treatment with ordinary etching reagents. The stability of these carbides under attack is of some importance in connection with the corrodibility of steels. Naturally this stability varies very much with the nature of the attacking medium (cf. attack of 3 per cent. sodium chloride solutions and 10 per cent. sulphuric acid upon steel No. 27). In this connection some information can be gleaned from the papers of Arnold and Read cited above.

The solid solutions on the whole are not structureless, but exhibit a small stippled appearance (this is seen in Figs. 7 and 10 of Part I). An exception to this is found in the highest vanadium steel. In one of the steels (the highest cobalt steel, No. 66) a portion of the carbide has decomposed into ferrite and graphite. This is not an uncommon experience with certain steels, particularly if annealed. The nickel steels with about 0·8 per cent. of carbon are particularly prone to this precipitation. The result in the cobalt steel is that there is graphite lying enclosed as the kernel of a nut of solid solution of cobalt in iron.

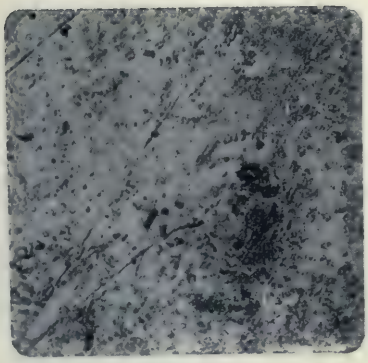
Throughout the series the grain size varies with the composition, the pure carbon steels having usually larger grains than the alloy steels. In the steels with only a small proportion of the third element, this change in grain size is slight or nil (except in the 3 per cent. tungsten series), but the large propor-

* *Journ. Iron and Steel Inst.*, 1910, I, p. 169; 1911, I, p. 249; 1912, I, p. 215; and *Journ. Mech. Eng.*, 1914, I, p. 223; 1915, I, p. 247.



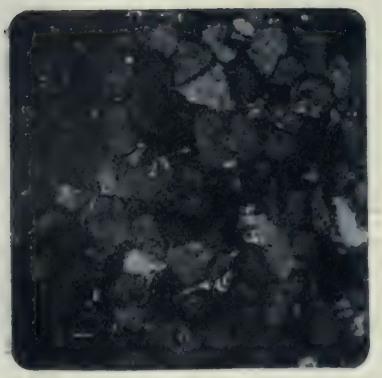
C 0·07, Ni 3·07.

FIG. 2.



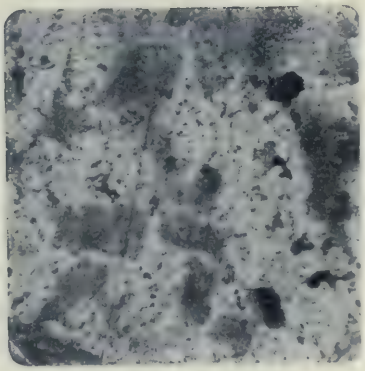
0·88, Ni 2·97.

FIG. 3.



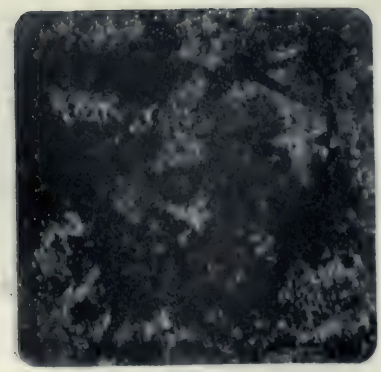
C 0·07.

FIG. 4.



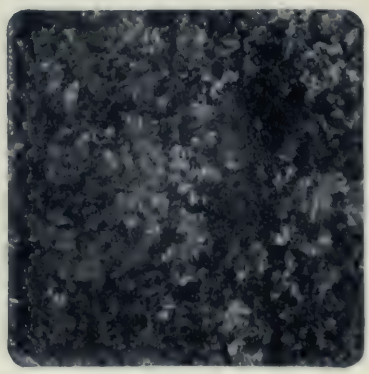
C 0·72, Co 20·85.

FIG. 5.



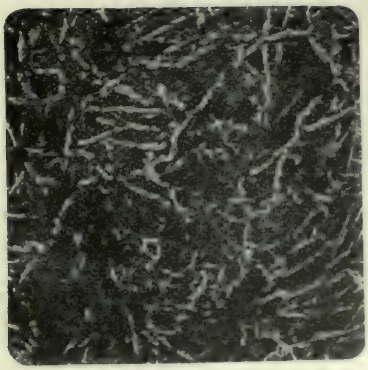
C 0·89.

FIG. 6.

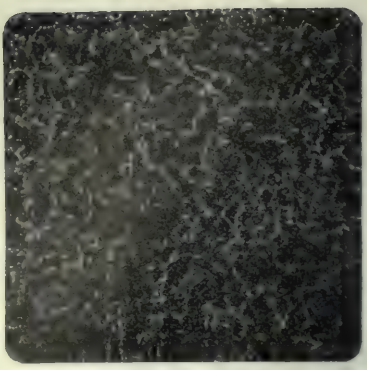


C 0·38, V 0·22.

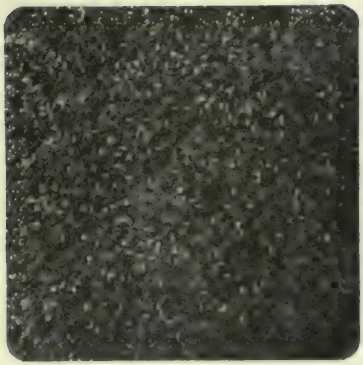
FIG. 7.



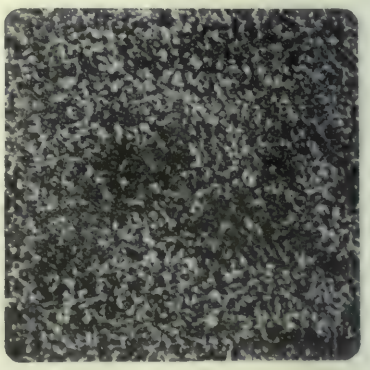
C 1·25.
FIG. 8.



C 1·30, V 0·21.
FIG. 9.

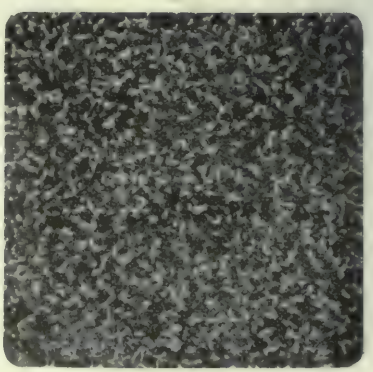


C 1·10, V 13·45.
FIG. 10.



C 0·72, W 5·37.
FIG. 11.

C 0·60, V 0·71.
FIG. 12.



C 0·74, W 14·96.
FIG. 13.

tion of tungsten or chromium or vanadium has produced a noteworthy difference (cf. Figs. 7 and 8). The series employed does not contain any steels showing troostitic or purely austenitic structures.

The question of mechanical strain due to either working or thermal treatment does not enter seriously into these steels, any strain resulting from the previous treatment of the steel having been eliminated from them as far as possible by the normalizing at 900° C. Some thermal strain must have remained after this cooling, but only such as is inherent to the cooling of all steels. A little mechanical strain is also bound to have been produced during the turning and polishing of the specimens, but this is almost unavoidable.*

Besides these factors that may enter into the corrosion effects, two others must be considered. The first of them is the inter-crystalline or inter-granular material found in various of these steels (e.g. those containing any large quantity of ferrite, and those with much solid solution and very little carbide). In particular this has been dealt with by Humfrey† and by Rosenhain and Ewen.‡ Both of these authors agree that the material is amorphous, but give different explanations of its formation. Humfrey maintains that these inter-granular volumes represent those portions of the mass where the regular arrangement of the molecules due to the orientation of one crystal is being gradually (more or less) changed to the different, orderly arrangement due to the orientation of the adjacent grain. On the other hand, Rosenhain and Ewen express the opinion that the space is simply filled up by excess matter from the crystals when the distance between the crystals has become too small for a continuation of a crystal growth in accordance with the orientation of the surrounding grains. Whichever, or whatever, explanation be accepted as the cause of this amorphous layer, its presence can hardly be doubted and its influence upon the corrosion cannot be neglected. The second remaining factor that may influence the behaviour of the steel when corroded is the possibility of twinning in the solid solution. This is usually confined to those materials possessing some grains of pure solid solution and no other constituent which can influence the growth of that particular grain. This structure was not apparent in any of the steels of the series; but one other containing approximately C 1·2 per cent., Mn 12 per cent., Si 0·35 per cent., S 0·03 per cent., P 0·06 per cent., and showing this type of structure, has been corroded in the manner described below.

Manner of Experiments and Results Obtained.—The sections taken from the bars after their normalization were polished in the usual way upon emery cloth and paper, and finished with diamantine powder upon moist, rotating, selvyt cloth. They were then dried with absolute alcohol and washed with ether. When quite clean and dry, they were immersed in a solution of 3 per cent. sodium chloride, being placed on the bottom of a glass crystallizing dish. After being immersed and left quite undisturbed in the dark for 10 days they were removed and washed in a gentle stream of tap-water, dried with absolute alcohol and examined under the microscope.

The results obtained show the utmost regularity. As might be expected, the ferrite is attacked in every steel of the series, though of course not to the same extent. It is fairly safe to assume that in every case the early stages of the attack are accompanied by the production of etching pits or their counterparts. This is well seen in the nickel steels Nos. 54 and 57 (Figs. 2

* This aspect of the question has been dealt with by various workers, cf. Heyn and Bauer, *Journ. Iron and Steel Inst.*, 1909, I, pp. 159–84.

† *Carnegie Memoirs, Iron and Steel Institute*, 1913, p. 86.

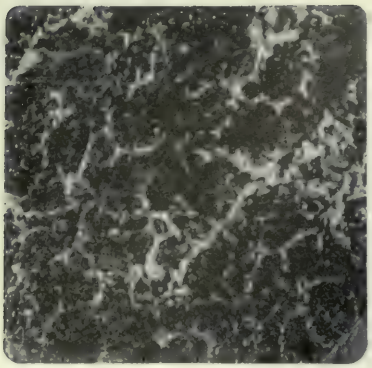
‡ *Journ. Inst. Metals*, 1912, II, p. 149 and 1913, II, p. 119.

and 3). In the bar iron which had been melted to remove the slag and which had only 0·07 per cent. of carbon, almost the whole is ferrite and the attack upon it may be seen in Fig. 4. This shows quite well that the different grains of ferrite corrode to an entirely different extent. The small white dots scattered sparsely over the field are cementite, and being segregated allow the material to act practically as though carbon free. From the figure it is plain that some grains have not been attacked at all, whilst others have been subjected to the attack of etching pits which have developed and deepened during the attack. In all those that have been attacked there is a rough or stippled appearance, showing the unevenness of the result of the attack in that particular grain, quite different from the appearance produced during an ordinary etching. The cobalt steel that contained some graphite has produced some ferritic material (containing cobalt, of course), and the attack on this may be seen in Fig. 5. Here the attack in the ferrite has been rather "patchy," and the boundaries of the grains are not at all so well marked as in the bar iron.

Curiously enough the pearlite, in practically every steel under review, is corroded so that it is practically indistinguishable from the ferrite. This is well seen in Fig. 6 (which is steel No. 10, containing 0·89 per cent. of carbon). It is hardly possible to pick out the boundaries of the grains in this steel, and in the grains themselves the attack is such as to leave no traces of the cementite, everything having been attacked. This is the result throughout the list of steels, it being next to impossible to distinguish any of the steels below 0·9 per cent. of carbon from one another. It also holds for the various alloy steels that contain pearlite. Fig. 7 (No. 39, having 0·38 per cent. of carbon and 0·22 per cent. of vanadium) shows no cementite of the pearlite still standing, but shows a preferential attack of some grains over the others. It is almost impossible to distinguish between ferrite and pearlite in this steel (as in the others). In the steels greater than 0·9 per cent. of carbon there is the same kind of attack, but rather intensified, the structurally free carbide having apparently helped the action considerably. This is seen very well in Figs. 8 and 9, representing steels Nos. 9 and 42, having respectively 1·46 per cent. of carbon and 1·30 per cent. of carbon with 0·21 per cent. of vanadium. The second case (Fig. 8) has probably more remnants of the pearlite structure than any other steel in the series. Fig. 12 (*infra*) also shows very clearly some of this remaining pearlite structure.

The structurally free carbides in the series show the greatest possible regularity. Throughout the list of steels under review, each carbide acts in the same way, being entirely unattacked. Whenever these carbides stand by themselves, whether as crystal boundaries and globules as the result of segregation, or in relatively large masses, the result is the same—they remain quite unattacked. This may be seen very well in Figs. 8 and 9 (*supra*) as illustrating the case of crystal boundaries, in Fig. 10 (No. 37, having 12·45 per cent. of vanadium), in Fig. 4 (*supra*) for the isolated globules, and in Fig. 11 (No. 46, having 5·37 per cent. of tungsten) for the large masses. The case of the segregated carbides is seen very well in the nickel steels, particularly Nos. 55 and 56, for there the pearlite and ferrite are corroded distinctly; but where there has been a separation of the pearlite into ferrite and cementite, the latter is quite unattacked. Also in Fig. 12 (No. 35, with 0·93 per cent. carbon and 5·84 per cent. vanadium) a certain amount of segregation has taken place, the result being that the carbide boundaries stand out alone and unattacked.

The solid solution which occurs in most of the alloy steels is also quite uniform in its behaviour. In general it is attacked fairly evenly, leaving the



C 0·73, W 21·5.

FIG. 14.

C 1·2 per cent., Mn 12·0 per cent.

FIG. 15.

free carbide which accompanies it, and which may be safely assumed to act as its electrical cathode, standing up quite alone and unattacked. The even attack is seen very well in Fig. 13 (No. 47, having 0·74 per cent. of carbon and 14·96 per cent. of tungsten), and the more uneven, due to the extra carbide dotted about in the solid solution, in Fig. 14 (No. 44, having 0·73 per cent. of carbon and 21·5 per cent. of tungsten). These two structures are quite typical of the steels containing solid solution and free carbides.

The influence of the inter-granular material referred to above is seen in several of the samples. The effect of the corrosion upon it is evident in Fig. 4. There may be noticed here, relatively broad black lines surrounding the grains. These are not optical effects at all, and in the actual specimen show up quite plainly and quite definitely. It seems fairly certain that this layer of material has been attacked preferentially at the commencement of the corrosion—or perhaps has been the centre of the action between the two adjacent crystals. Whatever the action may have been, it has resulted in the production of a narrow pit, the sides of which have been exposed. These sides are relatively rough and consequently offer a fairly large surface to the attack of the solution. In consequence there has been a relatively intense action in these regions. This would account for the slightly greater attack on the bar iron over that sustained by the steels with a higher carbon content. The inter-granular layer naturally does not appear in those steels having carbide boundaries to the crystals, but does appear in some of those steels having solid solution with very little free carbide, and that as globules scattered about within the grains (cf. No. 45 with 0·70 per cent. of carbon and 9·74 per cent. of tungsten, also in several of the chromium steels). The steel examined for the action of twinning was corroded in the same manner as the other steels, but it was found that the corrosion had gone on to a very great extent, the structure being entirely obliterated. (This is not due to the twinning alone, as a nickel steel possessing an almost identical structure did not corrode at all.) By corroding for a shorter period (three days) the structure shown in Fig. 15 was obtained. This shows that the parts of every steel orientated in different ways, corroded to different extents, though neither was quite free from attack. Evidently the existence of twinning is likely to hasten the corrosion of any material showing a tendency to be attacked.

The microscopic results coupled with the results obtained by the attack by the various corrosive media tend to prove the following interesting conclusions :—

1. That in ordinary metallurgical experience no steel is sufficiently homogeneous to be able to resist corrosive attacks. The most homogeneous material is the bar iron (No. 1), and yet this contains in itself the elements of a non-homogeneity (the amorphous inter-granular cement) which is sufficient to give it a very considerable corrodibility. Also that steels chemically homogeneous have not the true homogeneity that might be expected to furnish a resistance to corrosion, since they may possess twinned crystals which certainly aid corrosion, or may be in a state of thermal or mechanical strain.

2. That non-homogeneity is not in itself productive of a more easily corrodible steel. This is seen very well in the case of the chromium steel (No. 27, containing 19·46 per cent. of chromium) which is not corroded at all in the 3 per cent. sodium chloride solution, but which has a structure essentially non-homogeneous (composed of carbides and solid solution mixed together most intimately).

3. That the true secret of non-corrodibility lies in some property of the

solid solution—probably its solution pressure as reflected in its contact potential against the solution—which is to be found as a consequence of the chemical composition only, coupled with the thermal and mechanical treatment. Apparently iron itself is not capable of offering real resistance to corrosion because its solution pressure is never sufficiently low. It is hoped that the results of work in support of this view may be communicated shortly.

4. That carbides in steels act in two directions—(*a*) as deterrents, in that they resist corrosion in themselves, being quite unattacked by the majority of reagents ; (*b*) as aids in most cases, by providing a suitable cathode to act as counter to the anodic action of the ferrite in solid solution. In this latter way the presence of pearlite, which of course contains the carbide in considerable quantities, tends to increase the corrodibility of the steels. Although the pearlite appears in most cases to be attacked, it is most probable, in view of the persistence of the free carbides, that the attack is confined to the ferrite or solid solution. This latter, of course, constitutes the matrix in which the small rods or lenticles of carbide are embedded, and the disappearance of this support results in the mechanical removal of the carbide, and not in the solution or decomposition of it. This is supported by the fact that in every case of a metal containing any quantity of carbide (either free or in the pearlite), the sample after corrosion was covered with a loose layer of carbide that had to be removed before weighing. In the case of those pieces of carbide that are relatively large, it is quite conceivable that they are rooted so deeply in the ferrite or solid solution that the corrosion has not proceeded to the depth required to cause them to be loosened sufficiently to be removed by mechanical means. Similarly of course the boundaries of the grains are firmly fixed in the material and are not likely to be removed.

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ERRATUM.

In consequence of an uncorrected error the percentage compositions under Figs. 8, 10, *and* 12 *are incorrect. The correct compositions are given in the text where the Figures are mentioned.*

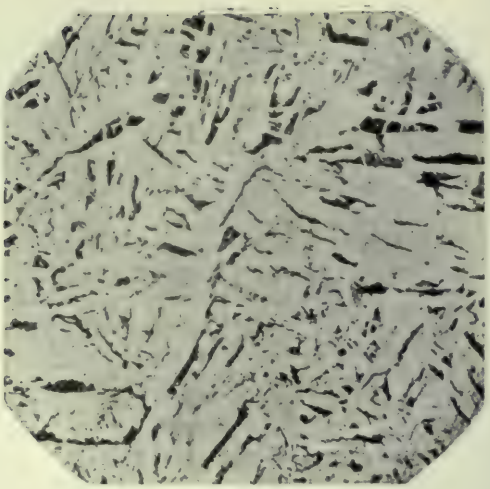


FIG. 1.

150 diam. Vertical illumination.

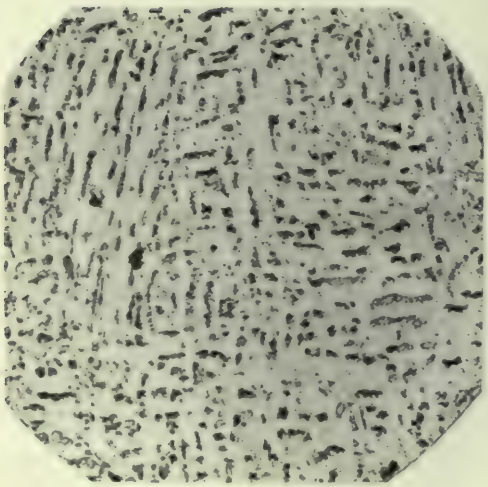


FIG. 2.

150 diam. Vertical illumination.

NOTE ON THE CORROSION OF IRON AND STEEL

Mr. S. Whyte, B.Sc. (Redhill), read a "Note on the Corrosion of Iron and Steel."

A case of rather rapid corrosion of a water-pipe recently came under the notice of the author. The pipe was made of the average quality of mild steel as far as chemical composition was concerned. When in use it was about 3 feet under the surface and in a soil of yellow clay. Corrosion had proceeded over the outside surface generally, and in places there were deep pits and in one place a perforation.

On micro-examination the steel was found to have a badly overheated structure, the ferrite having the form of straight bands with angular and elongated patches of pearlite between them. It was thought advisable to replace all the piping laid down at the same time as the bad one, but some of it when taken up showed much less corrosion, and in the latter case the only difference that was found was in the micro-structure and to the extent that the overheating had not been as bad.

Fig. 1 is a photomicrograph of the pipe which had corroded badly; Fig. 2 represents the pipe which had not corroded so badly.

While there is practically no relation between acid-corrosion and atmospheric tests, the author thought an accelerated test of some sort might give some valuable information on the effect of overheating.

When studying the corrosion of copper alloys, Dr. Desch and the author had found that the use of an electromotive force gave satisfactory results in examining the initial stages of corrosion.* Consequently, the light thrown on the mechanism of corrosion in its early stages enabled the subsequent chemical and mechanical actions occurring under service conditions to be foretold with some degree of confidence.

It was thought the application of this method in the above instance might be helpful.

The experimental method is the one employed on former occasions with the improved form of apparatus† to give more accurate measurements.

The specimen to be examined is made the anode, whilst the cathode is a small square of platinum gauze. The electrolyte, which is a dilute solution of sodium chloride, is allowed to remain in contact with the metal for a definite time and is then withdrawn and analysed. The electromotive force was obtained from an accumulator and was kept constant by means of a sliding resistance and voltmeter. Iron only was estimated in the corrosion product, and the coloration method with ammonium thiocyanate was used.

Two steels were chosen of ·28 per cent. C and ·55 per cent. C respectively. These were overheated at about 1,100° C. and cooled slowly. Portions

* C. H. Desch and S. Whyte, *Journal Institute of Metals*, 1913, x. 304. S. Whyte and C. H. Desch, ibid. 1914, xi.

† S. Whyte, ibid. 1915, xxxiv. 258.

were cut off and refined by reheating and then cooled in the same way. Specimens of accurate dimensions were prepared from the above and corroded under identical conditions. A series of results under varying e.m.f.'s and durations of tests show that the corrosion product from the overheated specimens is on an average about 20 per cent. more than that from the normalized ones.

Microscopical observations show that the free ferrite is first attacked, and on further corrosion a reversal takes place and the pearlite becomes relatively more attacked. This was observed by Dr. Desch and the author on a former occasion,* when the reversal corresponded to a maximum in the extraction of manganese by the electrolyte. On still further corrosion the free ferrite is again attacked relatively more than the pearlite and much more so in the overheated specimens. In a two minutes' test the ferrite of the normalized specimens was 1·5 thousands mm. below the pearlite areas, while in the overheated specimens it was 2·2 thousands mm. below.

As the difference of electric potential between adjoining crystals stimulates corrosion along the boundaries, it might be that the increase in the boundaries due to overheating is responsible for the increased amount of corrosion. Also in the reversal action, when the free ferrite is attacked in preference to the pearlite, the ferrite lamellæ of the pearlite is protected by some sort of local polarization, so that in a normalized steel, when the free ferrite and pearlite are intimately intermixed, the tendency would be to form the maximum number of those local couples, and thus give a minimum of corrosion.

Although the above method points to an increase in the amount of corrosion due to overheating, it is clear this method is only suitable for examining the initial stages, and it is possible that the subsequent mechanical actions might possibly reverse this, but the grain of the overheated steels being coarse and open, the chemical products of corrosion are not likely to be so adherent as with fine-grained specimens, so that it is probable the subsequent actions are more or less on a parallel with the initial ones.

DISCUSSION.

The President said that it would be convenient at this stage to take the discussion on the group of Papers dealing with Ferrous Metals, and he called upon Dr. W. Rosenhain to open the discussion.

Dr. Walter Rosenhain, F.R.S., said the question of corrosion was undoubtedly one of the most serious problems which had to be faced. Its seriousness was impressed upon him last year in connection with probably the longest water-pipe in the world, namely in Western Australia, which supplied the goldfields of Kalgoorlie ; corrosion in a steel structure of that kind was a very serious matter. In that case, water was being dealt with which had a particularly strong action on iron and steel. As regards the President's remarks upon the ancient specimens of iron and steel, possibly their owner might be warned a little as regards their corrosion-resisting properties. It was true that they had lasted well enough in Egypt, but would they last so well in London? He himself had a number of specimens of ancient iron from Adam's Peak in Ceylon, from the chains which assisted the

* C. H. Desch and S. Whyte, *Journal West of Scotland Iron and Steel Institute*, 1914.

pilgrims of the olden days to climb the mountain. They were worn round and smooth, and apparently uncorroded. He had cut a section of this iron and had found that in the air of his laboratory, which was as pure, if not purer than most London air, it rusted very badly. The same thing had happened whenever ancient iron was exposed to modern air—the two did not agree. Perhaps the owner of the Egyptian specimens might be induced to cut a small piece off for testing in this way. He believed that ancient iron when first made contained a great deal of cinder, and possibly these layers of cinder were nearly, if not quite, continuous in places. The iron corroded down to these layers and then corrosion stopped. In the chains he had spoken of this was obviously the case in one or two places. The outside surface was simply a surface of cinder protecting the iron beneath. Otherwise there was no magic about this iron at all. It had been protected by the circumstances of the case, and under modern conditions corroded just as badly as modern iron. He believed the resistance to corrosion of the so-called stainless steels, also referred to by the President, was to some extent dependent upon the surface condition in the same way. He had had occasion to examine a steel of a somewhat similar type of American origin. This had been sent over as a "rustless" steel, but it had been necessary to scrape the rust from the surface before it could be analysed. Nevertheless, a polished specimen of that steel remained absolutely bright and untarnished for months, yet when the surface was roughened it rusted. The surface condition played a very important part, and he was inclined to speculate about it and suggest that the surface amorphous layers possibly contained a protective element.

He was greatly interested in both Mr. Aitchison's papers, and there were one or two things which were suggestive. The decrease of corrosion with the increase of carbon up to 0·35 per cent. or 0·4 per cent. was extremely interesting. It was, he believed, the second property of steel which reached a critical point at that concentration. Benedicks had pointed out another, and he (Dr. Rosenhain) desired to draw attention to the coincidence—if it was a coincidence—that this was the concentration at which the transformation into beta iron ceased. Mr. Aitchison had also referred to intercrystalline cement, and the work which he and his collaborators had been doing led him to attach some weight to that hypothesis; but there were difficulties in the way of Mr. Aitchison's views. That author stated that the grain size had no relation to corrosion, yet admitted that corrosion was influenced by this intercrystalline cement, whatever its nature might be. These two statements did not appear to be quite compatible, because if this intercrystalline influence caused corrosion, there should be a relation between grain size and corrosion. Mr. Whyte's evidence to some extent supported this, but he was rather afraid of that evidence, because he did not know whether the material was in the normal state or whether there had been a burning action resulting in a chemical change which might have played some part in the phenomenon which Mr. Whyte had observed. He would like to see the actual photomicrographs of the two pipes. It was, however, an interesting and unique case. Finally, all laboratory experiments on corrosion had to face this criticism, namely, that it was only possible to work on the beginning of corrosion. It had been shown that it was the final rate of corrosion which mattered, when it was considered that the life of a piece of steel of material thickness was not proportional to the rate at which corrosion commenced. That was probably the greatest objection to the electrolytic theory of corrosion of Cushman and Walker, since steel which was reluctant to commence corrosion might yet corrode

very quickly once it had begun. Some nickel steels behaved in that way, and it was necessary to be cautious in drawing conclusions from these experiments.

Sir Robert Hadfield, speaking with regard to Dr. Rosenhain's reference to the corrosion of "stainless" steels, referred to the information given in his own Paper of the two specimens Nos. 1176 M and 1177 M, which thoroughly confirmed what Dr. Rosenhain had said, namely, that a roughened portion was much more inclined to corrosion than a smooth portion.

Mr. L. Pendred said that some three years ago, in conjunction with Mr. Harbord, he undertook a series of tests on a considerable scale. Most tests on corrosion had been carried out by laboratory methods, but the object in the series to which he had referred was to conduct tests on what might be called commercial or industrial lines. They took large pieces of steel, in most cases 12 inches square, and left them in the condition in which they were received from the makers; the mill scale was not removed. About ten steels were taken in all, two of each kind — basic Bessemer, acid Bessemer, acid open-hearth, and so on. They also took some iron from two makers, namely Lowmoor and Roundoak. Three plates of each kind were exposed under different conditions. They wanted to find out, as Dr. Friend had asked, whether any particular kind of steel made by any particular process would be more resistive under certain conditions than others. A set of plates was exposed on the roof of Cannon Street Station, another in sea-water at Southampton, another in the Thames at Marlow, and another, a somewhat severe test, in a length of tunnel on the South-Eastern Railway; another set was exposed to exhaust steam, and finally a number of plates were exposed to London air on the roof of Mr. Harbord's office. Thus these experiments were on totally different lines from those usually adopted, and some mention of the results, which were disappointing but none the less useful, might be interesting. The intention, however, was to read a longer paper before the Iron and Steel Institute. Every individual plate was analysed carefully, and the analyses had been preserved. It was anticipated that by using plates of this large size, namely 12 inches square, some being $\frac{3}{8}$ in. thick, others $\frac{1}{4}$ in., and others less, that any small errors in weighing would cancel themselves out.

The results of the tests were inconclusive. It was hoped to find that either acid open-hearth, or acid Bessemer, or basic Bessemer, and so on might be more resistive to corrosion than any other kinds of steel. This they had been totally unable to find. The results on the average showed that all steels were about equally resistive, and that iron was no better and no worse than steel. It was found that one kind of acid Bessemer was bad, whilst another acid Bessemer was very good. One acid open-hearth gave equally good results with a basic Bessemer, whilst one make of basic Bessemer was a good deal worse than another make. One kind of iron gave excellent results, whilst another was nearly at the bottom of the lists. The conditions under which they were exposed also led to some curious and interesting results. Thames water had very little corrosive effect. (The President: Hear, hear.) London air was 15 to 20 times as bad as water, and even surpassed sea-water. The plates which were exposed to steam were placed in a large tank through which exhaust steam was sent for the greater part of a week and cut off every week-end. The plates were left in the damp atmosphere which collected at the bottom of the tank, and one would have thought there would have been serious corrosion. As a matter of fact, some of the plates showed no corrosion at all. The difference in them could not be weighed, whilst on the other hand nickel steel began to go to pieces

almost at once. In some cases corrosion began very rapidly, whilst other plates lasted for three years under these conditions without practically any loss. In the tunnel, which was a very severe test on account of the gases from the locomotives and the damp, all the plates gave equally good results, and there was nothing to choose between iron and steel. Exposed to water, iron was no better than steel.

Dr. T. M. Lowry, F.R.S., said that no reference had been made to the experiments of Moody and others, which had shown the important part played by carbonic acid in the rusting of iron. Ordinary rust was not merely an oxide or hydroxide, but contained a large proportion of ferrous carbonate. The curious arboraceous growths of rust which had been illustrated by Friend and by Heyn were easily explained as a result of the precipitation of rust by the oxidation of ferrous bicarbonate. In one of Moody's experiments iron nails, submerged in water, were covered with a filter-paper, and the rust then appeared on the upper side of the filter-paper and not on the nails at all, thus proving clearly that it had been precipitated from solution.

Mr. A. F. Dismore suggested that corrosion should be dealt with not as taking place from the outside to the inside, but from the inside to the outside. He claimed to have proved it possible to convert cast iron with a high percentage of carbon into steel which was practically non-corrodible. A cast-iron plate having a tensile strength of 9 tons had by an electrolytic process of his own been converted into a metal having a tensile strength of 45·1 tons. He showed a number of specimens, and mentioned that tests carried out by Messrs. Riley and Harbord and Messrs. D. Kirkcaldy and Sons confirmed what he had said. He had reason to believe that the Germans had already begun to work in the direction he had indicated as regards corrosion, and it was the knowledge of this that had induced him to hurry up and patent the process he had mentioned, and which he had hit upon accidentally. It was possible to take a plate of cast iron which could be corroded with rust in a matter of three hours, yet small specimens of similar material after treatment by his process had been left lying about for several years and nothing had happened. A number of specimens were exhibited, and the process was explained as an electrolytic one in which a current of from 250 to 440 volts was employed.

Sir Robert Hadfield explained that he could not in any way vouch for the results. Whilst the experiment was no doubt important, he could not without fuller investigation determine its value. There were many eminent scientists present, and he would like them to hear about the process. Mr. Dismore had sent him two specimens, one stated to be before and the other after treatment. In the former there were high silicon, high phosphorus, and high carbon, and the material was unquestionably cast iron. After analysis it was found that the graphite had disappeared, leaving 0·35 per cent. carbon. The phosphorus had also to a large extent disappeared. Such change seemed difficult to account for. This was why he left it to Mr. Dismore to make his own explanation. Could he explain the method?

Mr. Dismore said the method had come to light quite accidentally in the course of working the process known as black nickelling. He was testing a liquid with the object of filling in the pitted marks in planished iron. A piece of cast iron was placed in the liquid, and subjected to a voltage, and he was astonished at the result. Since then further pieces had been tested, and Messrs. D. Kirkcaldy had given certificates of tests they had carried out. One of these stated that the cast iron had a tensile strength of 9·9 tons, but that after treatment this was increased to 35·1 tons with 15 per cent. extension

in four diameters. The appearance of the fracture was silky. An analysis by Messrs. Riley and Harbord showed that a specimen before treatment had 3·044 carbon and only 0·150 after treatment. The graphitic carbon before treatment was 2·734, after treatment nil. The carbonized carbon before treatment was 0·320, after treatment nil; silicon before 3·29, after 0·021; sulphur before 0·076, after 0·092 (a slight increase); phosphorus before 1·619, after 0·092; manganese before 0·317, after 0·385 (this increase he could not account for); nickel before 0·042, after 0·040. His experiments had proved beyond doubt that the centre of the material was attacked first, and he had come to the conclusion that in the case of corrosion the same working takes place, viz. outwardly from the inside.

The President: Can you give us the specific gravity before and after treatment?

Mr. Dismore: Not at present.

Mr. Arnold Philip said that the expression "ordinary tap-water" was somewhat vague, but he presumed that Mr. Aitchison was referring to Sheffield town water, which was a very soft water. (Mr. Aitchison: Yes.) Such water, due to the fact apparently that it contained free carbonic acid gas, caused far more trouble from corrosion than was the case with the tap-water supplied in the South of England, which was usually hard, and often very hard when obtained from the chalk.

Dr. Friend and Mr. Aitchison employed different units for measuring corrosion. At present there seemed to be as many units as there were investigators. It was very much to be hoped that some agreement would be arrived at to adopt a unit which could be accepted generally.

Dr. Allerton S. Cushman (Washington), in response to an invitation to contribute to the discussion, wrote to say that he had read the various Papers with the greatest interest. The point that appeared most prominently in the discussion seemed to be whether or no any good purpose was served in making elaborate series of corrosion tests by determining loss in weight of test pieces after immersion in dilute acids, salt solutions, or other corroding media. Mr. Aitchison's Papers showed confidence in such methods of testing, and that author, in summing up, expressed the belief that the results obtained by the attack by the various corrosive media tend to prove interesting conclusions. Dr. Friend had given qualified endorsement to similar methods of testing in his statement that *in the absence of pitting the results are trustworthy and of great value.* Dr. Friend, had, however, immediately afterwards pointed out the often unknown factors that affect weight losses under such test conditions, and had conservatively warned that *the final appeal must always be made to the results of experience and of experiments carried out with a liberal hand on a large scale under actual working conditions.* Sir Robert Hadfield, in the opening address at the general discussion, had pointed out certain discrepancies noted between dilute acid immersion tests made by different experimenters on duplicate samples of the same steels. Nevertheless, Sir Robert Hadfield betrayed in his address some measure of confidence in the results of such tests, as he refers to a certain steel as not showing satisfactory corrosion resistance in 10 per cent. sulphuric acid solution. Dr. Desch, on the other hand, had ranged himself very definitely against this method of testing, in stating that: "Such tests are usually of an unsatisfactory character, inasmuch as a number of metals or alloys, arranged in order of their resistance to acid solutions, will present a very different order when exposed to technical conditions." He (Dr. Cushman), as the result of many years of study on complex corrosion problems, had reached the conclusion that tests based upon the loss of weight of small samples immersed

in corrosive liquids were worse than useless, and were, in fact, pernicious, inasmuch as they led investigators to wrong and misleading conclusions. Considering acid tests alone, the results are profoundly influenced by the quantity and character of very small amounts of impurities in both the acid and the test pieces. The question as to whether there were traces of arsenic in the test acids would have such an effect that it might induce one experimenter to conclude that a given metal or alloy was highly resistant to corrosion, while another experimenter might reach an opposite opinion. On the other hand, two test pieces cut from the same plate or sheet might very possibly, on account of segregation or strains, show widely divergent degrees of excellence in the same liquid under the same conditions. Corrosion goes on under a system of complex and very sensitive reactions that are unquestionably affected by the catalytic action of impurities present both in metal and medium. It is well known that every catalyst has its poisons and its stimulants, so that everywhere that corrosion is going on there is a complex equilibrium of unknown factors at work, and, moreover, the equilibrium is constantly changing and readjusting itself from time to time. This is clearly shown by the fact that iron does not ever rust at a given rate—the corrosion goes on by fits and starts, now accelerating and now slowing down, affected by the changing conditions of day and night, winter and summer, dryness and moisture, variable catalysis, etc. Thus, flakes of iron-rust are always laid up in well-defined strata, indicating intermittent formation. All these considerations, the truth of which cannot be gainsaid, show the futility of drawing very fine distinctions between one metal and another as the result of immersion tests, whether in the laboratory or in the open. The only rational test is a service test, and even this should be interpreted conservatively and in the light of experience, as Dr. Friend has so well stated.

All these considerations would appear to make the investigation of corrosion problems a discouraging field to enter. It should be remembered, however, that great variation in excellence undoubtedly exists in this respect as between different types and makes of metal, and it is legitimate to inquire into the reasons for these differences. If an experimenter were presented with strip samples of platinum, nickel, copper, and iron, and were asked to grade them as to corrosion resistance by laboratory methods, he would find little difficulty in arriving at a correct result. When, however, a number of samples of types of irons and steels and ferrous alloys are put in competition, the problem narrows down and becomes most difficult. As an instance of what is meant, he would call attention to the results of Mr. Aitchison's immersion tests on 3 per cent. nickel steels, which lead to the conclusion that over a wide range of carbon content 3 per cent. nickel steels are more corrodible than ordinary steels. These results are quite out of accord with his own (Dr. Cushman's) observations on large-scale weather tests extending over five years, in which the 3 per cent. nickel alloys have given such a good account of themselves that only the high cost of production has prevented their manufacture in America.

One great difficulty in forming conclusions based on loss of weight of test samples lies in the fact that the conclusion is often exactly the opposite of the desired truth. It must not be forgotten that when a metallic surface is being eaten away by corrosion, electrolysis is always at work. If any point or zone of an immersed metallic surface has a higher solution pressure than neighbouring or surrounding surface areas, the given point or zone will be electro-positive and will dissolve and pit rapidly. At the same time the electro-negative area is being protected and is not losing weight at all.

If he had succeeded in making himself clear, it would be seen that possibly the samples which lose the least weight are the most undesirable. We could remove considerable weight from a plane surface of metal with a piece of emery cloth, without doing the least damage, whereas very little weight taken out from one place with a drill would ruin the surface. If the intention was, for instance, to select the best steel for a turbine blade, we would not care in practice if it lost a little weight evenly over its entire surface, but we would be much concerned if it corroded unevenly on its knife-like edges. Or, again, as Dr. Friend points out, an iron boiler might lose pounds in weight and yet be little the worse, whereas the loss of an ounce in one place might lead to a tragedy.

Dr. Friend had referred to varying colour of iron rusts produced in different corrosive liquids. He (Dr. Cushman) had been paying particular attention to the colour of rust formed on commercial full-sized corrugated test sheets which had been exposed to the weather for varying lengths of time up to very nearly five years. The present indications are that, after the lapse of several months, the darker the adherent rust, the more rust-resistant and the longer lived will be the sheet under weather exposure conditions. It is characteristic of Bessemer steel sheets, under atmospheric exposure, to show a tendency to cover themselves with a light, limonite-coloured, loosely adherent, granular rust preliminary to their final disintegration. Some open-hearth sheets show a similar condition, but very pure, carefully made mild steels and irons cover themselves with a closely adherent, fine-grained, chocolate-brown rust. Such sheets are invariably longer lived, and he (Dr. Cushman) was inclined to the opinion that the comparative excellence of individual test sheets could be judged by the colour and texture of the rust produced, although the prevailing nature of the atmosphere at the place of testing was also a factor in modifying the rust colour and texture.

In seeking a reason for this difference in behaviour between Bessemer and open-hearth sheets, the question of gas content immediately presents itself, and it is noteworthy that up to the present time few investigators have discussed relative corrosion resistance of irons and steels in the light of their possible gas content. He had been paying especial attention to this subject for some time past, and was being led to the belief that it is one of the prime factors in the corrosiveness of ferrous metals. Various gases may associate themselves with steel in three separate ways. They may be present in blow-holes, in the occluded form sometimes spoken of as solid solution, or in the combined form as hydrides, nitrides, or carbonyl compounds. A carefully made, properly degasified metal, as free as possible from segregation, is demanded if long life in service is the principal object in view.

He believed that many earnest investigators had deceived themselves to the point of concluding that a little copper, say a quarter of 1 per cent. or less, as an alloying constituent conferred resistivity on a steel, whereas in reality the secret lies in the attention given to purity and care in the manufacture, leading to a homogeneous, highly degasified metal. If this proves to be the truth, there is no reason for wasting perfectly good copper by melting it in as a constituent of steel.

He was grateful for the opportunity of entering this interesting discussion before this Society, and he hoped in the not distant future to prepare a detailed paper setting forth the results of his observations during the past three years.

Dr. J. Newton Friend, in replying, said that it had been suggested by Carulla in 1908 that possibly a reason for ancient iron being apparently

incorrodible was that stone anvils were used and some particles of the stone had got into the steel and gave a siliceous coating. In reply to a question put by Professor Carpenter the iron he had referred to was Kahlbaum's electrolytic. As to the necessity of a standard method of measuring corrosion, he thought his own, of taking a constant of 100, was the simplest. It was then easy to arrive at a corrosion factor for metals that corroded more quickly or less quickly. The same constant of 100 could also be applied to pitting, whereas Mr. Aitchison's method could not.

Mr. L. Aitchison, in his reply, stated that the criticism brought forward by Dr. Rosenhain was hardly just. The variations in grain size that were observed in the series of steels examined were due to differences in composition, and no observations had been made upon the influence of a variation in the grain size of the same material induced by heat treatment or by mechanical work. Also, practically the whole of the steels in the series contained carbides (and that not usually as eutectic), and this type of material has not yet been examined in the light of the various hypotheses accounting for the intergranular cement. In consequence it did not seem quite reasonable to compare the results obtained upon the relatively pure bar iron with those materials which contain a second and quite different constituent in large quantities. If the influence of a variation in grain size in the same material could be examined in a trustworthy manner, it is extremely probable that the relationship indicated by Dr. Rosenhain would be established.

THE ZINC-COPPER-COUPLE HYPOTHESIS OF BRASS CORROSION.

Mr. Arnold Philip (Admiralty Chemist, Portsmouth) read the first of the group of Papers dealing with Non-Ferrous Metals, entitled "The Zinc-Copper-Couple Hypothesis of Brass Corrosion."

Many investigators have attributed the corrosion of two-phase brass by sea-water to the action of small electrolytic currents set up by minute couples of adjacent crystals of metal of different phase,* and it has been suggested that even grains of differently oriented crystals of a single phase may act in the same manner.

As far as the author is aware, it has not, however, yet been suggested that the corrosion of commercial brass consisting of the α, the α and β, and the β phases may be due to the action of minute zinc-copper couples functioning as small electrical cells all over the surface of the brass. It is to this view that it is now desired to call attention. It has long appeared to the author that much might be advanced in support of this idea, and the present opportunity appears advantageous for bringing forward some of the facts which seem to lend probability to the zinc-copper-couple hypothesis.

As a preliminary it must be remarked that hitherto the author has not been successful in devising any completely convincing test which will demonstrate by itself that the corrosion of brass when immersed in an electrolyte is due to the action of zinc-copper couples on its surface, but on the other hand he has been equally unsuccessful in obtaining definite evidence that this action does not take place. Nevertheless, the explanations which this hypothesis offers of many peculiarities of brass corrosion, when considered as a whole, do give a considerable amount of circumstantial evidence in its favour.

Both the α and the β phases of brass consist of solutions of zinc in copper, and no direct evidence of any chemical combination between the two elements is known to exist.†

The surface of such brass may therefore reasonably be considered to consist of surfaces of zinc and copper in close contact.

The corrosion of industrial brasses, whether carried out electrolytically by an external electromotive force or by any other means, has never been known to cause the separation from the brass of any other metal or intermetallic phase except copper. It has repeatedly been shown that although under suitable conditions copper may be separated from brass under a process of dezincification, the metallic corrosion residue always consists of (*a*) the unaltered brass or (*b*) pure metallic copper or a mixture of both.

The foregoing facts may be considered to furnish an indication of the possibility, if not the probability, that brass corrosion may be due to the mutual electric action of the copper and the zinc contained in it as such in the presence of an electrolyte.

* Milton and Larke, *Proceedings of the Institution of Civil Engineers*, vol. cliv., p. 27, 1903.

† Carpenter has claimed that the β phase consists of a mixture of the α and the γ phases, but as far as is known this view is regarded by other investigators as not yet fully established.

The behaviour of brass immersed in an electrolyte may be conveniently considered under three principal heads :—

1. *Auto-corrosion*, due to the action of an electrolyte upon brass immersed in it out of contact with any other electrically conducting body.

2. *Contact-corrosion*, due to the action of an electrolyte upon brass immersed in it when the brass is in contact with some other solid conductor also immersed or partially immersed in the electrolyte.

As examples of such other conducting solid bodies the following may be considered :—

(*a*) A more electro-negative solid than copper, as, for instance, coke.

(*b*) Copper.

(*c*) A less electro-negative solid than copper, but more electro-negative than zinc, as, for instance, cuprous oxide.

(*d*) Zinc.

(*e*) A more electro-positive solid than zinc, such as, for instance, magnesium.

3. *External current corrosion*, due to the action of an electrolyte upon brass immersed in it when an externally generated electric current flows through the surface of contact between the brass and the electrolyte. This current may pass—

(*a*) From the brass into the electrolyte, or

(*b*) From the electrolyte into the brass.

I. The Auto-corrosion of Brass.

Take the first case, that of the corrosion of brass immersed in sea-water without contact with any other conducting solid body. Here, if the zinc-copper couples' action is the cause of corrosion, a current flows from each zinc element, zinc chloride being formed, to each copper element, where caustic soda is formed and a certain amount of hydrogen is deposited on the copper ; if no depolarizing material such as oxygen is present in the water, the action quickly ceases, due to polarization, and we have the case of a piece of brass immersed in sea-water free from oxygen, and under these circumstances, as has been repeatedly shown experimentally, no corrosion loss or dezincification occurs. If, however, sufficient oxygen is present in the water to just oxidize the hydrogen as it is deposited, the current continues at its highest possible value and a maximum corrosion of the zinc occurs, whilst the copper being just protected from oxidation, marked dezincification is observed. If, on the other hand, the supply of oxygen is in excess of that necessary to oxidize the hydrogen liberated by the corroding currents, the copper becomes oxidized to suboxide of copper. This substance, however, is less electro-positive than zinc but more so than copper, and hence the current flowing from the zinc falls in strength, whilst a small amount of current flows from the cuprous oxide areas to any copper areas, forming copper chloride from the copper oxide and depositing hydrogen on the copper.

The above statement of the zinc-copper-couple action will therefore cover the general case of the auto-corrosion of a piece of brass immersed in sea-water without contact with any other conducting solid. The phenomena which have been experimentally observed are :—

1. If oxygen is absent from sea-water no corrosion occurs.

2. If oxygen is present—

(*a*) Dezincification and separation of metallic copper may occur ; or

(*b*) Solution of the zinc and corrosion of the copper without the separation of copper ; or

(*c*) A combination of 1 and 2 in which both copper oxide and metallic copper are separated, whilst the zinc is dissolved.

3. If the temperature is raised with the same proportion of oxygen in the water, corrosion is accelerated, due to the fact that the conductivity of the water is increased whilst the e.m.f. of the zinc-copper couple is also raised, thus increasing the magnitude of the corroding currents.

4. If the strength of the electrolyte is increased, as when concentrated sea-water is used at either the normal temperature or at a higher temperature, we again have the corroding currents increased, because once more both the conductivity of the solution and the e.m.f. of the couple are raised. Conversely, if a diluted sea-water is used the corrosion is diminished.

5. If the oxygen content of the water is raised corrosion increases.

6. If the water is agitated corrosion increases, because, firstly, more oxygen is introduced, whilst secondly, the polarizing deposits and solutions of zinc chloride and caustic soda formed respectively at the surfaces of the zinc and of the copper are continually removed and replaced by the pure sea-water. It is observed in this connection that zinc in the zinc chloride solution formed and the copper in the caustic soda solution formed both give smaller e.m.f.'s than the same metals in the unaltered sea-water. This is also in accordance with the general law that the decompositions of an electrolyte in which any pair of electrically connected elements are immersed always lower the original contact e.m.f. at each element, and the same is also true of the material, if any (such as hydrogen on the copper), which is deposited by the current.

7. With dilute sea-water dezincification of brass is more marked than with the normal undiluted water.*

8. The rate of the auto-corrosion decreases as the duration of the corrosion increases.

Passing next from the general case of the corrosion of any alloy of zinc and copper containing only the α, α and β, or β phases to the particular cases of the auto-corrosion of two copper-zinc alloys, one containing a higher percentage of zinc than the other, we find that the higher the percentage of zinc present—

(*a*) The lower is the rate of corrosion for sea-water containing a given oxygen content; † and

(*b*) The greater tendency there is for dezincification to appear. ‡

In connection with the fact that their observation showed repeatedly that Muntz metal corroded more slowly in normal stagnant sea-water at ordinary temperatures than was the case with 70/30 brass under the same conditions, Messrs. Bengough and Jones remark: "These results are surprising. In the first place it would be expected that the Muntz metal tube would suffer the greatest loss of weight, since it is a two-phase system and would therefore appear to be peculiarly liable to electrolytic action. . . . The 70/30 brass is a homogeneous single-phase system and would be expected to show less loss of weight." The present writer would be inclined to agree fully with these investigators' conclusions if the corrosion of brass is to be considered as being due only to the electric couples formed by different phases of the copper-zinc alloys. If, on the other hand, the action is considered as being due to electrolysis produced by zinc-copper couples, an opposite conclusion must be arrived at.

For if a mass of brass is acted upon by an electrolyte so that the metallic zinc is corroded away, the corrosion loss consists not only of the zinc dissolved away and the copper which has been chemically attacked, but also of the

* Bengough and Jones, *Journal of the Institute of Metals*, vol. x., p. 40.
† Ibid., 1913. vol. x., p. 32. ‡ Ibid., pp. 40 and 41.

spongy copper remaining, if any dezincification has taken place. Hence in a 70/30 brass, if 30 parts of zinc are dissolved, 100 parts of brass are corroded and destroyed, whilst in a 60/40 brass, if 30 parts of zinc are dissolved, only 75 parts of brass have been destroyed. Thus, if a piece of 70/30 brass and a piece of 60/40 brass are both suspended in the same sea-water, but are not in contact with each other or any other conducting body, and if it is supposed that the molecular currents from the zinc-copper couples per unit area of the surface in contact with the sea-water of each of the samples is the same, it must be admitted that the weight of zinc dissolved per unit area per unit of time must be the same for both the 70/30 brass and for the 60/40 brass, and therefore, from what has been said above, the weight of the 70/30 brass destroyed per unit area per unit of time must be greater than the weight of 60/40 brass destroyed on the same area in the same time in the ratio of 100 to 75 or 1·3̇.

But, further than this, consideration will show that the molecular currents from the zinc-copper couples per unit area of the 60/40 brass cannot be equal to the similar molecular currents per unit area of the surface of the 70/30 brass : for each unit of area of zinc in the copper-zinc couples on the surface of 60/40 brass has a corresponding area of copper in approximately the ratio of 1 of zinc to 1·5 of copper, but in the 70/30 brass the ratio of the zinc to the copper areas is approximately 1 : 2·5. Hence in 60/40 brass under corrosion in sea-water, for a given amount of molecular current from the zinc-copper couples per unit of area of brass surface a greater amount of hydrogen is deposited per unit area of copper, and hence more polarization must occur than is the case where a 70/30 brass is corroded in the same solution.

Not only this, but as the oxygen which acts as a depolarizer performs this function chiefly on the surface of the copper, if the surface of the copper is reduced the depolarization becomes less active.

For both these reasons it is clear that the molecular corroding currents from the zinc-copper couples per unit area of the surface of 60/40 brass when immersed in sea-water must be not equal to but must be less than the similar molecular currents per unit area of 70/30 brass corroded under the same conditions.

Hence the ratio of the destruction of 70/30 brass per unit area to that of 60/40 brass when both are exposed for the same time to the same electrolyte is not only in the ratio of 1·3̇, as has been shown would be the case if the zinc-copper-couple currents were equal per unit of surface area exposed to corrosion, but must be something greater than this by an amount which it is difficult to calculate theoretically.

Messrs. Bengough and Jones, in the Second Report to the Corrosion Committee of the Institute of Metals, have published several results of pairs of simultaneous corrosion tests on 70/30 brass and on 60/40 brass in both normal sea-water, diluted sea-water, and concentrated sea-water at both atmospheric and also at higher temperatures. Each pair of tests was carried out under identical conditions. Calculations made from these results, which are summarized in the tabular statement on the next page, show that the values of the ratio of the corrosion rate of 70/30 brass to that of 61/39 brass under the various conditions of test used vary from about 1·55 to 2·19, whilst the minimum theoretical ratio for these two alloys is over 1·30 as shown above.

The zinc-copper-couple hypothesis not only offers an explanation of the more rapid auto-corrosion of the copper-rich commercial brasses which has been experimentally observed, but it also indicates that it is to be expected that under similar conditions as to the amount of oxygen present in the water dezincification is more likely to be noticeable in the zinc-rich brasses than in

Calculated Values of the Ratio of the Auto-corrosion per Unit Area per Unit Time of 70/30 Brass to that of 61/39 Brass in Sea-water, from Messrs. Bengough & Jones's Results as given in the Second Report to the Corrosion Committee of the Institute of Metals.

1	2	3	4	5	6	7	8	9	10	11
Page.	Table.	Duration of Corrosion in Days.	Temperature of Water.	Condition of Water.	Strength of Sea-water.	Position of Test Pieces.	Distance of Test Piece below Surface of Water.	Loss of Weight per cent. of—		Ratio of Loss given in Column 9 to that given in Column 10.
								70/30 Brass.	61/39 Brass.	
24	II	208	18–20° C.	Stagnant	Normal	Vertical	½ inch	0·50	0·31	1·61
24	III	208	,,	,,	,,	,,	3 inches	0·45	0·27	1·66
35	IV	120	,,	,,	,,	Horizontal	1 inch	0·56	0·36	1·55
40	VI	168	,,	,,	Equal parts of sea and distilled water	Vertical	½ inch (?)	0·57	0·30	1·90
52	VIII	35	40° C.	,,	Normal	Horizontal	1 inch	0·24	0·11	2·19
52	VIII	35	,,	,,	,,	,,	,,	0·21	0·11	1·90

As the thickness of the brass upon which these tests were made was uniform, the loss of weight per cent. given in columns 9 and 10 is proportional to the loss of weight per unit area, and hence the ratio given in column 11 is actually the observed value of the ratio of the corrosion loss per unit area per unit time for 70/30 brass to the corrosion loss per unit area per unit time for 61/39 brass. The theoretical minimum value of this ratio for 70/30 brass and 61/39 brass is 1·33.

The page and table numbers given in columns 1 and 2 refer to vol. x. of the *Journal of the Institute of Metals*, 1913.

the copper-rich brasses. For, given an equal volume of current per unit surface area when two brasses of different copper content are immersed in the same sea-water, the surface of the copper being smaller in the zinc-rich brass will be more densely coated with hydrogen and will therefore be more fully protected against the action of the oxygen, the available amount of which for hydrogen-oxidation purposes must also be less, for it must be a function of the area of the copper exposed to its action, and this is less. It is therefore to be expected that a brass of high zinc contents will be more likely to exhibit signs of dezincification than one of low zinc contents, and this, as has already been pointed out, has been observed to be the case by Messrs. Bengough and Jones.

It is of interest to attempt to make some estimate of the magnitude of the total zinc-copper-couple corroding currents which may flow per unit of surface area during the auto-corrosion of brass in sea-water. One method of making such an estimate is to calculate the total zinc lost in a given time per unit area of surface during auto-corrosion in sea-water. The most active rate of loss of weight of brass which the author has repeatedly observed in running aerated sea-water for a period of 60 days is of the order of 30 grains per square foot of surface exposed to corrosion per 100 days. If the brass is a 70/30 brass, this corresponds to a corrosion loss of 9 grains of zinc per square foot per 100 days, and this loss is equal to a current of 0·0002004 ampere per square foot of surface. Calculations made from other data given later on depending upon the corrosion of brass by an externally generated e.m.f. have shown that the magnitude of the auto-corrosion current per square foot may vary between 0·000346 ampere to 0·003174 ampere.

The mean value of the auto-corrosion currents per square foot of surface per 100 days' corrosion must of course vary with the period over which the corrosion takes place, as it is recognized that the corrosion losses are greater per unit of surface per unit of time for short than for long periods, whilst the rate of supply of oxygen and variations in temperature and rate of circulation of the water also affect the magnitude of the rate of corrosion and hence also of the mean value of the zinc-copper-couple corroding current per unit area.

If the e.m.f. of a brass-zinc couple immersed in sea-water is measured by a zero-current method by either an electrostatic voltmeter or by a potentiometer method, it is found to be less than that of a copper-zinc couple in the same solution and at the same temperature. It might therefore be argued that the brass cannot consist of a mixture of zinc and copper elements as such, but must consist of some chemical compound of zinc and copper differing both from zinc and copper.

But this conclusion may be seen to be unwarranted if one considers two sheets of copper A and B and one sheet of zinc C, all immersed in sea-water and all insulated from each other (Fig. 1). If suitable means are taken to measure the potential difference between A and B, it is found to be zero, and between A and C it is that of a zinc-copper couple for the given electrolyte at the given temperature; but if now B and C are electrically connected, a local current flows between them and a layer of zinc chloride solution is formed over the surface of the zinc and a layer of caustic soda solution is formed over the surface of the copper, and the difference of potential between the connected sheets of copper B and zinc C and the sheet of copper at A is found to be less than if the copper at B were not connected to the zinc C, due not only to the fact that the electrolyte over the surface of the copper and of the zinc at B and C is no longer sea-water, but also partly to the fact that a local current is flowing between the copper B and the zinc C.

Marked and sharply localized dezincification areas in brass have repeatedly

been noticed by many observers to occur beneath white crystalline deposits of what appears to be a basic chloride of zinc, which are formed upon the surface of brass when corroded in sea-water. It is a peculiarity that this type of dezincification proceeds somewhat rapidly.

If the formation of these deposits has once occurred, and if one admits that beneath them there is a somewhat strong solution of zinc chloride, it is considered that the observed rapid dezincification of the alloy can be explained on the zinc-copper-couple hypothesis, for if the strong zinc chloride solution possesses a higher conductivity than normal sea-water, and if the oxygen available is sufficiently large in amount to destroy or partly destroy the hydrogen deposited on the copper, the conditions for rapid dezincification are present.

But the full consideration of this particular form of dezincification is not yet possible, owing to the fact that suitably devised experiments upon it have not yet been carried out. How are these crystalline deposits of basic zinc chloride first formed? Are they caused in the first instance by a preliminary dezincification which their presence then accelerates, or are the crystals first deposited on some rough surface and do they then initiate the acute dezincification? Do the crystals in fact initiate the dezincification, or does the dezincification initiate the crystals?

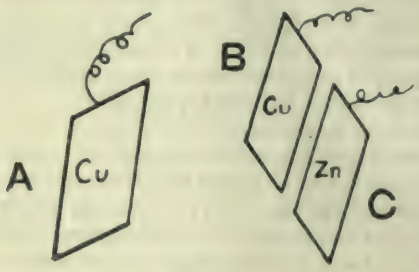


FIG. 1.

The author's opinion on this point at present is that it is a mutual action, and therefore tends to take place on a roughened surface or upon points or edges of a sample of brass. More investigation on this phenomenon is desirable, and one or two peculiarities which it presents may be remarked upon. Bengough and Jones * have observed with regard to this action that it occurs more readily in brasses containing high zinc contents—that is, in two-phase structures—and have also found that it occurs more readily at high than at low temperatures, whilst, what is particularly remarkable, these investigators find it to occur more readily in sea-water diluted with an equal volume of distilled water than is the case if sea-water only is used.

The same investigators have also observed that zinc chloride crystals when placed in contact with a brass tube at ordinary temperatures do not produce dezincification, but that when heated to 70–80° C. marked dezincification appears.

As far as the author is able to follow Messrs. Bengough and Jones's work on the dezincification of brass, he gathers that they have never observed dezincification without at the same time observing an overlying white crystalline deposit of basic zinc chloride. The author, on the other hand, believes that he has observed dezincification without any appearance of zinc chloride

* Loc. cit.

crystals ; but this may be due to the fact that the crystals were there, but were of so microscopic dimensions that their presence was overlooked. The relationship between dezincification and these crystals deserves further investigation.

In so far as what the author terms the auto-corrosion of brass is concerned, the zinc-copper-couple hypothesis appears to be in contradiction of the fact observed by Chief Engineer Isherwood, of the United States Navy, that the corrosion per unit surface area of thick brass is less than the corrosion per unit area of thin brass exposed to sea-water under the same conditions of time, temperature, oxygenation, etc.* It must, however, be stated that it is not known that Isherwood's experiments on this point have been confirmed or contradicted by results obtained by any other observer.

The zinc-copper-couple hypothesis of corrosion also does not appear to offer any explanation of the fact observed by O. Sackur † that brass alloys of high copper content will not deposit metallic copper from solutions of certain copper salts, although brasses of lower copper contents will deposit copper from the same solutions.

Experiments on the behaviour of brass in solutions of both copper and zinc salts are now being carried out by the author in order to ascertain as to whether this aspect of the question will give any useful indication as to an experiment which will finally settle this matter in one sense or another.

It has often been noticed in the course of experiments on the corrosion of brass in sea-water that a rough surface tends to cause more marked corrosion, and it is considered that the peculiarity is sufficiently accounted for on the zinc-copper-couple hypothesis of brass corrosion if it is considered that due to roughness of the copper surface the polarization of the copper is decreased for a given oxygen supply in the electrolyte because the hydrogen deposited by the current and oxygen deposited from the sea-water both tend to collect at rough points, i.e. points of maximum curvature, and hence the two gases, the polarizer and the depolarizer, are brought into contact with each other, and the resultant destruction of the hydrogen prevents the decrease of the corroding current which would otherwise occur on a smooth surface.

II. The Contact-corrosion of Brass.

If, as shown diagrammatically in Fig. 2, two pieces of copper sheet, Cu_1 and Cu_2, and one piece of zinc sheet, Zn_1, are immersed in an electrolyte and are connected by the wires *a*, *b*, and *d*, which are all out of contact with the electrolyte, whilst the three galvanometers A, B, and D are placed in circuit with each of the wires, and if there is an open contact key at P, then before this contact is closed it will be observed that the currents passing through *a* and *b* as read by the galvanometers A and B are equal. If now the key at P is closed, the current passing through the wire as read on the galvanometer A is found to have increased, whilst the current passing through the wire *b* as read on the galvanometer B is found to have decreased, and a current now flows through the wire *d* as shown on the galvanometer D, and this current is the difference between the currents in A and B which flow after the key at P is closed.

This simple experiment illustrates the action of the contact-corrosion of brass when the brass is electrically connected with a mass of copper, Cu_2. The current through the zinc, Zn_1, in the brass has been increased from

* G. D. Bengough, Report to the Corrosion Committee of the Institute of Metals, 1911.

† O. Sackur, *Berichte der Deutschen Chemischen Gesellschaft*, 1905, **38**, 2186.

the value it had before being connected to the copper, Cu_2, and hence its corrosion is increased proportionately. That is, the auto-corrosion current has been increased to a contact-corrosion current which has a greater magnitude.

If in Fig. 2 the resistances of the connecting wires and of the circuits through the electrolyte are denoted by the letters a, b, d, f, and g, as shown, and if the resistance of the galvanometers is imagined to be zero, the resistances a and b will represent the resistances of the contact of a contiguous pair of zinc, Zn_1, and copper, Cu_1, particles on the surface of a piece of brass exposed to corrosion in contact with a mass of copper, Cu_2, both immersed in any electrolyte, whilst the resistance d is the resistance of the contact between the brass and the mass of copper, Cu_2, and finally f is the resistance through the electrolyte between the copper mass, Cu_2, and the brass, and g is the resistance through the electrolyte between the particle of copper, Cu_1, and the contiguous particle of zinc, Zn_1, on the surface of the brass. A simple calculation shows that the current flowing between the contiguous particles of zinc, Zn_1, and copper, Cu_1, before closing the key at P is $\frac{e}{a+b+g} = A$, where e is the zinc-copper-couple e.m.f. in the particular electrolyte.

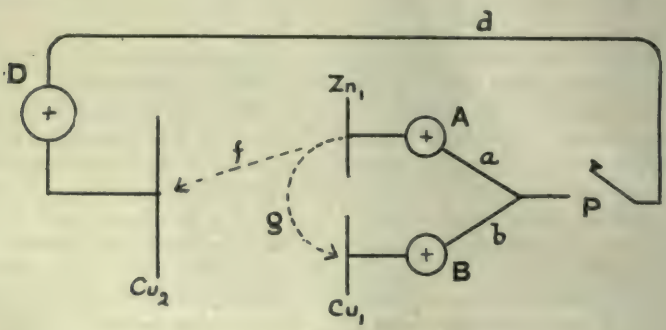


FIG. 2.

This current then represents the auto-corrosion current from a unit zinc-copper couple and corrodes the zinc. The expression for this current depends only on the nature of the electrolyte as represented by the e.m.f. e and by the resistance g of the path of the current through this electrolyte, and on the thickness and nature of the brass plate that is on the resistance of the path of the current through it which is represented by the symbols a and b.

After the larger mass of copper, Cu_2, has been placed in contact with the brass by closing the key at P, the current from the zinc rises to

$$A_1 = \frac{e}{a + \frac{(d+f)(b+g)}{b+g+d+f}}.$$

Or, as b and g are constants it is simpler to write $(b+g) = K$, when the auto-corroding current from the zinc becomes

$$\frac{e}{a+K} = A,$$

whilst the corroding current from the zinc, when put into contact with the

copper mass, Cu_2, i.e. when the brass is put into contact with the copper becomes

$$a + \frac{e}{\frac{(d+f)K}{K+d+f}} = A_1,$$

and the increase of the zinc corroding current is

$$= A_1 - A = a + \frac{e}{\frac{(d+f)K}{K+d+f}} - \frac{e}{a+K} = \frac{eK^2}{a^2K + aK^2 + (d+f)(a+K)^2}.$$

All the quantities involved in this expression for the increase of the zinc auto-corroding current caused by its contact with the mass of copper, Cu_2, are constants except d and f. These are respectively the resistances of the metallic connection between the copper, Cu_2, and the brass, and the resistance of the path through the electrolyte between the copper, Cu_2, and the brass, and

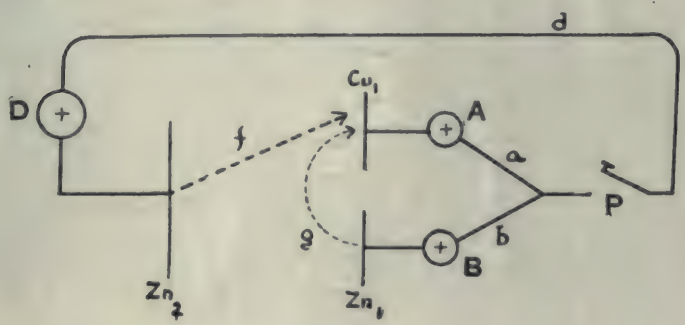


FIG. 3.

it is evident that the smaller either or both of these quantities are the greater will be the current A_1, and therefore the corrosion of the zinc caused by the contact between the brass and the copper, Cu_2. The limiting maximum value of this current when $d = f = 0$ is therefore $\frac{e}{a}$.

In order to secure the maximum corrosion due to copper in contact with brass it is therefore necessary that the contact between the brass and the copper should have as low a resistance as possible, and the area of the copper exposed to the sea-water should be as large as possible, and the distance between the copper and the brass through the electrolyte should be as small as possible.

In precisely the same manner the decrease in current through the zinc of the brass, and therefore of corrosion of the brass which is caused by connecting the brass to a mass of zinc in the sea-water, may be observed experimentally if the circuits are arranged as shown in Fig. 3.

Before closing the key at P the currents A and B in the resistances a and b are equal, but on closing the key at P the current in a increases from A to

A_1, and the current in B decreases from B to B_1, that is, the corrosion of the zinc decreases from its auto-corrosion value—

$$\frac{e}{a + b + g} = B$$

to a smaller value—

$$e \left\{ \frac{d + f}{a(d + f + b + g) + (d + f)(b + g)} \right\} = B_1 ;$$

but, as before, b and g are constants, and if $(b + g) = K$, the zinc current through b, after closing the key at P, falls to

$$B_1 = e \left\{ \frac{d + f}{a(d + f + K) + (d + f)K} \right\},$$

and the amount of decrease is

$$B - B_1 = \frac{aK}{(a + K)^2 (d + f) + aK(a + K)} ;$$

and as all the quantities in this expression are constants except d and f, it is evident that the smaller either d or f or both are made the greater will be the reduction of zinc corrosion in the brass caused by connecting the brass to a mass of zinc. In the best conceivable case for a zinc mass electrolytically protecting brass from corrosion, d and f could in the limit both be zero, and the zinc auto-corroding current would then also become zero, that is to say, the brass would be completely protected from corrosion ; but as a matter of fact neither d nor f can be reduced to zero, and in most cases f must be moderately large, therefore the corrosion current practically can never fall to zero, and the contact of a mass of zinc with brass in an electrolyte cannot completely protect it from corrosion. But in all the foregoing remarks no consideration has been paid to the fact that an alteration of the polarization of the copper may occur by the deposition of hydrogen on the copper in larger or smaller amounts than is the case when the mere auto-corrosion is taking place.

This alteration of polarization does, as a matter of fact, occur. The increased current to the copper in the brass when the brass is in contact with a mass of zinc covers the copper areas in the brass more completely for the same conditions of electrolyte and temperature, etc., than when auto-corrosion only is taking place : hence the zinc corrosion currents not only fall by the amount shown above, but they decrease by a greater amount, and may reduce the zinc corrosion currents practically to zero, in spite of the fact that d and f have some reasonably high values.

The effect of the contact of solid conducting bodies which possess either a higher negative contact e.m.f. with sea-water than is the case with copper, as, for instance, coke, or a higher positive contact e.m.f. with sea-water than is the case with zinc, as, for instance, magnesium, or, finally, with such a body as cuprous oxide, which possesses a contact e.m.f. with sea-water which is intermediate between the values given by zinc and copper under the same conditions—the effect of such contacts is similar in its nature to that caused by the contacts with zinc and copper respectively as considered above, except that the increase of the zinc corrosion currents is more marked with coke than with copper, and, moreover, direct electrolytic solution of the copper takes place, whilst with magnesium (which has not, however, been experimented with) no doubt the protective layer of hydrogen formed by zinc protectors on the copper of the brass is extended to the surface of the zinc in the brass.

III. The External Current Corrosion of Brass.

The simplest case to consider is that in which the current flows from some suitable anode in the electrolyte to the brass: here it deposits both caustic soda and hydrogen, and effectively protects the brass from further corrosion.

This is the process used commercially under the Cumberland method for protection from corrosion. Useful and interesting as this method of combating corrosion is believed to be, it has, as far as the author is aware, little or no light to throw upon the validity or otherwise of the copper-zinc-couple hypothesis of corrosion of brass, and therefore no further remarks need be made concerning this case of the effect of currents on brass corrosion.

The second case, in which an externally generated current passes from brass into an electrolyte, is, however, of a good deal of importance, and has been studied by Milton and Larke,* and in more detail and more recently by Desch and Whyte.†

This aspect of brass corrosion is of much interest as bearing upon the zinc-copper-couple hypothesis. For if an electric current flows from a brass surface supposed to consist of contiguous areas of zinc and copper, and if the current density is sufficiently high, it must be regarded as flowing not only from the zinc areas, but also from the copper areas; and as under these circumstances no hydrogen is liberated at these surfaces, no question of polarization can occur due to hydrogen on either the zinc or the copper. Further, as each area of zinc and each area of copper possesses a distinct contact e.m.f. with the electrolyte, and as this e.m.f. is greater with the zinc than with the copper, it is to be anticipated that the current density of the current leaving the zinc will be greater than that leaving the copper, and therefore that for equal areas of copper and zinc the rate of solution of the zinc will be greater than that of the copper, and that therefore dezincification will occur and copper will be separated in the metallic form.

If now the behaviour of a copper-zinc alloy, such as Muntz metal, containing both the α and β phases is considered, it must be concluded that the electrolysis of the metal must be concentrated on the phase richer in zinc, that is, on the β phase.

These conclusions therefore indicate (1) that the α phase should be more slowly attacked than the β phase (which is the reverse of what occurs in auto-corrosion), and (2) that in both cases when attack takes place dezincification should also occur, whilst (3) when a brass containing both the α and the β phases is corroded the β phase should be first attacked.

But these are the actions which Desch and Whyte's experiments show take place.

The above remarks as to the theoretical method by which the electrolytic corrosion of brass should take place, as based upon the zinc-copper-couple hypothesis, apply of course only to the initial action, for as copper is set free the fraction of the corroding current borne by the zinc must decrease for any given phase, and the ratio of the copper to the zinc appearing in the solution as corrosion products must therefore increase as the duration of the corrosion increases.

And this is exactly what Messrs. Desch and Whyte's results show to be the case. In their first paper on this subject‡ they give a series of results of the corrosion of a sample of β-phase brass having the composition 52·92 per cent. copper and 47·05 per cent. zinc.

* *Proceedings of the Institution of Civil Engineers*, vol. 154, p. 4, 1903.

† "The Microchemistry of Corrosion," Part I, *Journal of the Institute of Metals*, No. 2, 1913, vol. x., p. 304; Part II, Whyte and Desch, No. 1, 1914, vol. xi., p. 235; Part III, Whyte, No. 1, 1915, vol. xiii., p. 80.

‡ *Journal of the Institute of Metals*, No. 2, 1913, vol. x., p. 313, Table V.

In this series of tests the same anode of brass was corroded successively for six periods of 5 minutes each, and in each period a fresh quantity of 5 c.c. of a 5 per cent. solution of sodium chloride was used as the electrolyte. The anode was not cleaned in any way between the tests. The ratios of the copper dissolved to the zinc dissolved in each of these successive periods were as follows :—

	Ratio of Copper dissolved to Zinc dissolved.
1st period	0·02457
2nd period	0·02457
3rd period	0·05320
4th period	0·07092
5th period	0·1176
6th period	0·1852

Messrs. Desch and Whyte also found that cored structures in the α phase were most markedly corroded on the zinc-rich portions.

In their second paper on this subject Messrs. Desch and Whyte state* that the experiments which they have made confirm them in their opinion that there is no essential difference between the process of electrically stimulated corrosion (i.e. what the present writer terms external current corrosion) and natural corrosion (i.e. auto-corrosion), and that consequently the method of electrical corrosion they have described may be employed for the purpose of determining the probable order of resistance of alloys to corrosion. The present writer does not, however, fully agree with this view, although he considers that it is more nearly correct if referred to a comparison between the effects to be expected from what he has termed the contact-corrosion of brass with coke and external current corrosion.

The very detailed results of the external current corrosion experiments given by Desch and Whyte in the three papers they have published state in every case the total weights of both zinc and copper which either passed into solution or were altered from the metallic to the oxidized or combined form, and it has therefore been possible to calculate the actual currents which must have passed from the brass into the electrolyte both from the copper and from the zinc areas of the surface of the brass (that is, assuming the copper-zinc-couple hypothesis to be correct), and as the areas of the anodes are given and the compositions of the brasses and the density of both copper and zinc are known, it has also been possible to calculate the current density in the zinc areas and the current density in the copper areas and the mean current density in the whole anode used. Further, from these results the values of the auto-corrosion currents in amperes per square foot of anode surface have been calculated, and for 70/30 brass have been found to vary from 0·000346 to 0·003174. These results are of the same order as the value for the auto-corrosion current per square foot of 70/30 brass which was calculated from other 60-day auto-corrosion data, namely 0·0002004.† But the values as calculated from Desch and Whyte's results, in which the exposure to corrosion in sodium chloride solution occupied only 60 minutes at the longest, are markedly higher than in those calculated from the 60-day auto-corrosion of 70/30 brass in sea-water. As, however, the mean rate of auto-corrosion of a brass decreases markedly with the length of the period of corrosion, it is to be expected that the mean auto-corrosion current per square foot, when obtained from auto-corrosion lasting for a period of

* *Journal Institute of Metals*, No. 1, 1914, vol. xi., p. 245.

† Vide *supra*, p. 249.

60 days, should be lower than the mean auto-corrosion current per square foot of anode calculated from corrosions lasting usually only 5 minutes, and at the most never more than 60 minutes, as was the case in Desch and Whyte's experiments.

In conclusion, it is observed that theoretically the variation of voltage upon the electrolytic corrosion of brass should cause the nature of the corrosion to vary in a definite manner, assuming the zinc-copper-couple hypothesis of brass corrosion to be correct. Experimental investigation of the effect of his variation of voltage is now being carried out by the author, and it is hoped that the results can shortly be reported.

The permissible limits of time and space do not allow of a more complete development of the facts at present known which bear upon the corrosion of brass as regarded as being due to metallic couples, but it is submitted that the facts here put forward do prove that undoubtedly such corrosion can only be explained by the action of metallic couples. This view does not, however, necessitate the further conclusion that these metallic couples are copper-zinc couples, but as this latter hypothesis explains several facts, which the assumption that couples are formed of different phases of the copper-zinc alloys does not do, and as zinc and copper are not necessarily in a state of chemical combination in either the α or the β phase, it is considered that much probability at present attaches to the zinc-copper-couple hypothesis of brass corrosion.

THE CORROSION OF A SOLID SOLUTION—70/30 BRASS.

Mr. W. E. Gibbs, M.Sc. (Special Lecturer in Metallurgy, Liverpool University; Acting Honorary Investigator for the Corrosion Committee of the Institute of Metals), dealt in his Paper with the Sea-water Corrosion of 70/30 Brass.

[*Note.*—The sea-water corrosion of brass condenser tubes has recently been investigated by Dr. G. D. Bengough and Mr. R. M. Jones. The results of their work are contained in the Second Report to the Corrosion Committee of the Institute of Metals. This Report is published *in extenso* in the *Journal of the Institute of Metals*, 1913, vol. x. The present author was appointed to assist Dr. Bengough in the early part of 1914. When war broke out Dr. Bengough accepted a commission in the Royal Garrison Artillery, and the work of the Committee was placed temporarily under the direction of the author. It is hoped that a Third Report will be presented to the Corrosion Committee in the spring of 1916. Most of the work upon which the present Paper is based will be found in detail in that Report. The present scheme of investigation has been greatly aided by the able experimental work of the assistant investigator, Mr. R. H. Smith. The author wishes to acknowledge his indebtedness to the Corrosion Committee of the Institute of Metals for permission to make use of the unpublished matter included in this Paper.]

When an alloy of copper and zinc is immersed in sea-water, it may corrode uniformly in three ways:—

(*a*) It may lose both constituents simultaneously and at the same rate. Both copper and zinc are then found in the corrosion product and in the proportions in which they are present in the original alloy. This is called "complete" corrosion.

(*b*) It may lose one constituent only, either copper or zinc. The corrosion product will then contain copper or zinc—not both. This is called "selective" corrosion.

(*c*) It may lose both constituents simultaneously but at different rates. The corrosion product will then contain both copper and zinc, but in a ratio which is different from that in which they occur in the alloy.

In addition to these three types of uniform corrosion, localized action may occur at various points of the metal surface. This localized action may be "complete" or "selective." If the first, it produces a pit; if the second, it produces spongy copper or an alloy richer in zinc. Very frequently in practice these products of a selective local attack are worn away mechanically, and the final result is as in the case of "complete" localized corrosion—the formation of a pit.

Some of the many factors which determine the character of a corrosive attack are :—

(*a*) The composition of the alloy.
(*b*) The temperature.
(*c*) Aeration of the sea-water.
(*d*) The concentration of the sea-water.
(*e*) The catalytic action of oxysalts of zinc and copper.
(*f*) The physical condition of the metal.
(*g*) Contact with electro-negative substances, such as carbon.

(*a*) *The Composition of the Metal.*—The rate of corrosion of copper in sea-water at ordinary temperatures is diminished by alloying it with zinc. This diminution increases rapidly as the proportion of zinc is increased until it reaches a minimum when the alloy contains an equal number of atoms of copper and zinc. Indeed, the alloy containing 50 atoms per cent. of copper and zinc appears to be almost unattacked by sea-water at ordinary temperatures.

When the alloy contains more copper than zinc, the proportion of copper in the corrosion product is rather more than in the alloy, i.e. the copper dissolves more rapidly than the zinc. It would seem that the rate of corrosion of pure zinc is diminished by the addition of copper in a correspondingly regular manner until it reaches a minimum at the alloy containing 50 atoms per cent. of zinc. In alloys containing more than this amount of zinc, the zinc dissolves rather more rapidly than the copper.

The curve showing the relation between the rate of corrosion and the composition of the alloy exhibits, during the first few weeks, a second minimum point in the neighbourhood of the 70/30 alloy. This, however, speedily disappears, and after ten weeks the curve exhibits the familiar deep U-shape, characteristic of the properties of a series of solid solutions. This curve is being redetermined by Mr. F. G. Martin and the author. It is proposed also to extend the investigation to higher temperatures. Loss of weight measurements are being supplemented by a careful analysis of the corrosion products.

(*b*) *The Temperature.*—The initial rate of corrosion of 70/30 brass in sea-water increases as the temperature rises from 15° C. to 50° C. Between 50° C. and 60° C. the initial rate of corrosion appears to fall off very quickly, for at 60° C. it is less than at 30° C.

In Table I is shown the loss of weight per week, in milligrams per square centimetre, of hard-drawn 70/30 brass in unaerated sea-water at 15° C., 30° C., 40° C., 50° C., and 60° C. during four successive weeks.

TABLE I.

Loss of Weight in mgm. per sq. cm.

Temperature.	15° C.	30° C.	40° C.	50° C.	60° C.
During first week ...	0·32	0·45	0·52	0·65	0·35
During second week	0·28	0·25	0·20	0·30	0·20
During third week ...	0·20	0·20	0·08	0·17	0·15
During fourth week...	0·16	0·16	0·04	0·12	0·10
During fifth week ...	0·14	0·12	0·12*	0·09	—

* Sea-water renewed for the first time.

The figures for 15° C. and 40° C. are calculated from the results given in the Second Report to the Corrosion Committee.*

In every case the rate of corrosion falls off with time, and more rapidly at higher temperatures than at low. Consequently, although the initial rate of corrosion is greater at higher temperatures, the actual rate of corrosion after a given time will be smaller.

Analysis of the corrosion product at 15° C. and 50° C. indicates that at these temperatures the attack takes place in three successive stages. First there is a slightly selective attack upon the copper. This is succeeded by a period of complete corrosion (after 9 days at 15° C. and 20 days at 50° C.). The third stage is an increasingly selective attack upon the zinc. In other words, at the beginning of corrosion the rate of solution of the copper is much greater than that of the zinc. This gradually falls off; at the same time the rate of solution of the zinc gradually increases. For a short time they are approximately equal. After that the rate of solution of the zinc is greater than that of the copper.

In stagnant sea-water this third stage occurs more quickly at 15° C. than at 50° C. It is probably dependent upon the amount of O and CO_2 present in solution in the sea-water. It is hastened by aeration. It appears to be associated with the formation of a film of copper oxide which protects the copper but permits solution of the zinc.

It is interesting to note, in connection with this change in the relative rates of solution of the copper and zinc of the brass, that pure copper dissolves readily in sea-water at first, but the rate of solution gradually diminishes owing to the formation of a protective film, possibly of oxide. Pure zinc in sea-water first becomes coated with a protective film of carbonate. This gradually undergoes some change (possibly it is transformed into oxychloride), and after a time the zinc dissolves in the sea-water at a gradually increasing rate.

In Table II are compared the changes in weight of a piece of pure copper and a piece of pure zinc in unaerated sea-water at 50° C.

TABLE II.

Change of Weight in mgm. per sq. cm.

Length of each Period in Days.	1.	4.	4.	4.	6.
Copper ...	−0·114	−0·356	−0·780	−0·500	−0·365
Zinc	+0·056	+0·475	−0·028	−0·190	−0·340

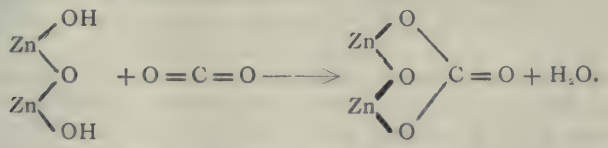
It will be noticed that the rate of solution of the copper begins to fall off after the first day, then increases during the third period, and after that falls off rapidly.

The zinc first of all gains in weight, owing to the formation of a film of carbonate. Afterwards it loses weight at a gradually increasing rate, although the white film still remains on the surface of the metal.

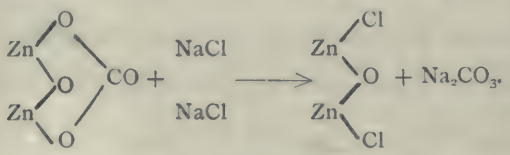
If zinc be immersed in sea-water which is free from CO_2 and aerated by CO_2-free air, it becomes coated with a film of zinc hydroxide, and no zinc oxychloride appears to be formed. On the other hand, it is found that sea-

* *Journ. Inst. Metals*, 1913, x., 46 and 52.

water aerated in the ordinary way produces on 70/30 brass a film of zinc carbonate and oxychloride. This is also found to occur with pure zinc. It would seem, therefore, that CO_2 is an essential factor in the formation of zinc oxychloride. It is conceivable that zinc in sea-water first forms a mixture of $Zn(OH)_2$ and $ZnO.Zn(OH)_2$, and that this with CO_2 forms zinc carbonate and an oxycarbonate, $ZnO.ZnCO_3$.



This oxycarbonate might then react, under certain conditions of salt concentration and temperature, with NaCl (or possibly with other chlorides present in the sea-water) to form zinc oxychloride, Zn_2OCl_2.



If the CO_2 concentration be sufficiently high the zinc will, of course, dissolve as zinc bicarbonate.

(*c*) *Aeration of the Sea-water.*—At the ordinary temperature aeration of the sea-water increases the initial rate of corrosion. At 50° C. its effect is very slight, while at 60° C. it diminishes the rate of corrosion. This is very well seen when the results contained in Table III are compared with those given in Table I.

TABLE III.

Loss of Weight (mgm. per sq. cm.) in Aerated Sea-water.

Temperature.	15° C.*	50° C.	60° C.
First week	0·80	0·62	0·11 gained
Second week	0·28	0·22	
Third week	0·24	0·18	0·01 gained
Fourth week	0·20	0·15	

It will be noticed that the rate of corrosion is greater in aerated sea-water at 15° C. than at 50° C.

The effect of aeration appears to be greatest at low temperatures. This is no doubt associated with the well-known fact that rapid localized corrosion occurs just inside the inlet end of the tubes in the coldest part of the condenser. In every case aeration increases the proportion of zinc in the corrosion product.

The corrosion of pure copper in sea-water is checked by aeration after a time owing to the formation of an oxide film. On the other hand, the corrosion of pure zinc in sea-water is considerably accelerated by aeration.

* Figures for 15° C. calculated from Second Report, *Journ. Inst. Met.*, x., 46.

There are two kinds of aeration—"gentle" aeration, in which the mechanical agitation of the sea-water by the stream of air is reduced to a minimum, and "violent" aeration, in which the stream of air either impinges directly upon the surface of the immersed metal or in some other way causes a violent agitation of the water immediately surrounding the metal. Dezincification of brass is accelerated very much by violent aeration, but to a much smaller extent by gentle aeration. Both kinds of aeration would occur in a condenser tube in practice—the violent aeration occurring just inside the inlet end.

(*d*) *Dilution of the Sea-water.*—Diluted sea-water attacks 70/30 brass more slowly than ordinary sea-water. At the same time the proportion of zinc in the corrosion product increases rapidly as the sea-water is made more dilute.

Thus after 34 days at 50° C. in gently aerated solutions of sea-water of the following concentrations, $\frac{S}{1}$, $\frac{S}{2}$, $\frac{S}{4}$, $\frac{S}{8}$, $\frac{S}{16}$ (where $\frac{S}{1}$ is the concentration of ordinary sea-water, $\frac{S}{2}$ being half that concentration and so on) the percentage of zinc in the corrosion products was respectively 18·0, 24·2, 33·9, 44·1, and 58·5. In $\frac{S}{1}$ and $\frac{S}{2}$ sea-water, therefore, the copper in the brass dissolves more rapidly than the zinc. But in $\frac{S}{4}$, $\frac{S}{8}$, and $\frac{S}{16}$ sea-water the zinc dissolves more rapidly than the copper.

This is in agreement with the general belief that estuary waters are more selectively corrosive than the water of the open sea.

The test-pieces used in this experiment were found to differ markedly from one another in appearance as the corrosion proceeded.

In ordinary sea-water the metal simply became covered with a uniform pale brown film. In $\frac{S}{2}$ sea-water a similar brown film was formed, but it was broken by a number of large areas of a reddish copper oxide, upon which, afterwards, a thin irregular deposit of a pale blue salt was formed. In $\frac{S}{4}$ sea-water the red oxide film extended over the whole surface of the metal. In this case, also, an irregular deposit of blue salt was formed. A number of minute white spots developed on the inner surface of this test-piece and were found to cover small areas of copper.

In $\frac{S}{8}$ and $\frac{S}{16}$ sea-water the character of the attack was not quite the same. Dull red oxide areas developed in places, but the rest of the surface appeared to be attacked very slowly and was quite unoxidized at the end of 34 days. No pale blue salt was formed on these test-pieces, but the surface of the test-piece in $\frac{S}{8}$ sea-water became dotted with small white spots, which were found to cover small areas of copper.

The appearance of the test-pieces, together with the results of the analysis of the corrosion products, show that in very dilute sea-water, such as $\frac{S}{16}$, the attack upon the copper is very greatly reduced. At the same time, however, the attack upon the zinc is not reduced; indeed, it appears to be slightly accelerated. It is clear, therefore, that the more dilute the sea-water the more favourable are the conditions for dezincification. It would be interesting to examine the corrosion of 70/30 brass in gently aerated distilled water.

The solubility of O and CO_2 is greater in diluted sea-water than in ordinary sea-water. It is possible, therefore, that the increased O and CO_2 content of the more dilute water, coupled with its diminished salt content, may play a part in facilitating dezincification. It has been found that distilled water contained in an open beaker and kept saturated with CO_2 will dissolve zinc from 70/30 brass (Ref. 1). This action is smaller at higher temperatures.

Air-free sea-water saturated with CO_2 in a closed vessel will dissolve zinc from 70/30 brass at the rate of 0·08 mgm. per sq. cm. in 20 days. No copper is dissolved, and the metal remains bright.

It has already been stated in this Paper that sea-water aerated by air which is free from CO_2 has very little action upon zinc. Clearly, therefore, CO_2 plays an important part in promoting the solution of zinc, and therefore in facilitating dezincification of brass. To what extent the influence of dissolved O and CO_2 upon the course of corrosion is affected by the concentration of the salts in the sea-water remains to be seen. It is well known that estuary and river waters generally contain more CO_2 and less O than the water of the open sea.

The solubility of pure copper in gently aerated sea-water is diminished by dilution of the sea-water and is least in distilled water. The solubility of pure zinc in sea-water is increased by dilution of the sea-water, and is greatest in distilled water. It appears from this that the dissolved salts are responsible for the solution of copper and the water and the dissolved gases for the solution of the zinc.

Dilution of the sea-water, therefore, while retarding the actual rate of corrosion of 70/30 brass, actively promotes dezincification.

(*e*) *The Catalytic Action of Zinc and Copper Oxysalts.*—Moist zinc chloride at ordinary temperatures does not produce dezincification. When heated to 70° C., however, rapid localised dezincification is set up, owing to the formation of zinc oxychloride (Ref. 2). When zinc chloride is added to sea-water at 40° C., in which a piece of 70/30 brass is suspended, it produces a finely divided white salt, zinc oxychloride, which gives rise to rapid dezincification of the brass (Ref. 3). Similarly at 50° C.

Aerated sea-water at 60° C. produces white spots on the surface of the 70/30 brass. These white spots are found to cover areas of copper, showing that they have produced dezincification.

Sea-water when allowed to dry on a piece of 70/30 brass at ordinary temperatures forms a greenish-blue crystalline salt which covers a pit. It does not appear to give rise to dezincification, but promotes rather the solution of copper.

Sea-water when allowed to dry on 70/30 brass at 100° C. forms a white salt which does promote dezincification.

At ordinary temperatures, therefore, the attack is greater upon the copper and the copper oxychloride is formed. This salt catalytically facilitates the solution of copper. At high temperatures (between 80° C. and 100° C. at any rate) the attack is almost completely upon the zinc, and zinc oxychloride is formed. This salt catalytically facilitates the solution of zinc.

In connection with this fact it is interesting to note the following experiment. A tube of 70/30 brass was heated internally by steam. Cold sea-water flowed continuously over the outer surface. At various points of the surface air-bubbles were formed. Where these air-bubbles appeared upon the surface of the hot tube, rings of zinc oxychloride were formed, presumably by the evaporation of the thin film of sea-water in the presence of the air of the bubble. In some cases a succession of air-bubbles had followed one another at the same point of the surface, each producing a ring of white salt

and so gradually increasing the deposit of white salt. This might be a frequent cause of localized dezincification in condenser tubes.

(*f*) *The Physical Condition of the Metal.*—When 70/30 brass is hard-drawn it corrodes less rapidly than when it is annealed. At the same time, however, there is a greater proportion of zinc in the corrosion product. Dezincification, therefore, occurs more readily in a hard-drawn 70/30 tube than in an annealed 70/30 tube. The loss of weight per week of hard-drawn and annealed test-pieces of 70/30 brass in unaerated sea-water at 30° C. and 50° C. for seven successive weeks is shown in Table IV.

TABLE IV.

Loss of Weight in mgm. per sq. cm.

	30° C.		50° C.	
	Hard.	Annealed.	Hard.	Annealed.
First week	0·45	0·50	0·65	0·95
Second week	0·25	0·45	0·30	0·28
Third week	0·20	0·43	0·17	0·13
Fourth week	0·16	0·40	0·12	0·09
Fifth week	0·12	0·35	0·09	0·07
Sixth week	0·11	0·30	0·09	0·06
Seventh week	0·08	0·28	0·08	0·04

It will be noticed that the rate of corrosion of the annealed metal falls off less rapidly than that of the hard-drawn metal, at 30° C., but rather more rapidly than it at 50° C.

(*g*) *Contact with Electro-negative Substances.*—Carbon, or coke, resting upon a clean brass surface, is generally in good electrical contact with the brass (Ref. 4). When good contact exists between the two, the rate of solution of the brass is increased fivefold, and the proportion of zinc in the corrosion product rises to 60 per cent. At the same time the surface of the metal becomes covered with a loosely adherent red film of copper oxide, which can be removed by a mere touch of the finger. The effect produced by contact with coke is much greater at 50° C. than at 15° C. The e.m.f. between coke and 70/30 is about 0·19 volt. Between coke and zinc there is an e.m.f. of about 1 volt, and between coke and copper about 0·16 volt. In every case the coke is the positive pole of the couple.

Other substances, electrically neutral, such as string or brick, act as loci for the accumulation of oxysalts of zinc and copper, and so lead to accelerated local corrosion.

A piece of coke fixed accidentally in a condenser tube might accelerate selective corrosion in four ways.

(*a*) If contact were good it would exert an electrochemical action.

(*b*) By obstructing the free passage of the water in the tube it would lead to a greatly increased temperature along that part of the tube between the coke and the inlet end. This would facilitate general dezincification of that portion of the tube.

(*c*) The water on the outlet side of the coke would only be able to trickle along the tube, and the continuous film evaporation to which it would be

subjected would, if the tube were hot enough, produce deposits of zinc oxychloride. This also would facilitate dezincification of the tube.

(*d*) By acting as a locus for the accumulation of oxysalts of zinc or copper.

Other cases in which corrosion, particularly selective corrosion, is localized at certain points along a condenser tube appear to be due to a lack of homogeneity in the metal itself. Perhaps local e.m.f.'s are set up between areas containing dissolved copper oxide and the remaining portion of the tube. The presence of strained metal in the hard-drawn alloy may be a contributory factor in the early stages of corrosion. It is generally noticed that the white spots of zinc salt, which indicate the occurrence of dezincification, always occur first along the drawlines and upon the filed edges of the test-pieces.

It is found that a small applied e.m.f. actively promotes dezincification. Such small e.m.f.'s might be set up in a condenser between unequally heated portions of the tube, or, under circumstances of good electrical contact, between the tube and the tube plate. It would be interesting to know the relation between the magnitude of the applied e.m.f. and the proportion of zinc in the corrosion product.

A general consideration of the foregoing facts conveys the impression that a solid solution of zinc and copper is intermediate in character between a physical mixture and a chemical compound. The copper and the zinc retain to a very large extent their own characteristic individuality, but in each case it is modified by the presence of the other constituent. It is as though there were some kind of weak chemical combination (or rather physical combination —since the chemical character of the constituents is not changed entirely but only modified) between the two, whereby the available energy of each is diminished.

In 70/30 brass the diminution of the available energy of the zinc is, of course, greater than in the case of the copper. For the influence which is exerted by a dissolved metal upon the character of the solvent metal is a function of the atomic volume. In the case of zinc and copper the atomic volumes are practically equal, and the influence of each constituent upon the other becomes a function of the concentration. When, however, the proportions of zinc and copper are equi-molecular, the available energy of both is reduced to a minimum, and the rate of corrosion at ordinary temperatures becomes practically zero.

In the alloys containing more than 50 atoms per cent. of copper it is the copper which dissolves at first, although zinc is more rapidly soluble in sea-water. This suggests that the chemical activity of the zinc is neutralized in the solid solution.

The electrode potential of zinc in sea-water at 16° C. is — 0·5100 volt, and of copper + 0·3896 volt. That of 70/30 brass is + 0·3460 volt, and therefore resembles copper rather than zinc. Similarly, the chemical activity of the copper is reduced considerably by the presence of the zinc in solid solution, and appears to reach a minimum when the atomic concentration of the zinc exceeds 50 per cent.

The strength of any combination between copper and zinc and the influence exerted by it upon the properties of the constituents would depend upon—

(*a*) The composition of the alloy. By which is meant the concentration of zinc and copper in the alloy and the presence of other metals, such as iron and tin, and of non-metals, such as oxygen.

(*b*) The physical state of the alloy, i.e. whether it is solid or liquid, amorphous or crystalline.

(*c*) The physical environment of the alloy, its temperature and pressure.

(*d*) The chemical environment of the alloy, which in this case refers to the nature and composition of the corroding solution.

Is it possible that a compound or compounds of copper and zinc exist stable only at low temperatures—say below 50° C.? These may dissociate into a system of solid solutions as the temperature rises and the composition is altered.

Such a conception appears to afford a reasonable explanation of the corrosion of 70/30 brass. Its application to other fields of investigation does not come within the scope of this Paper.

REFERENCES.

1. *Journ. Inst. Met.*, x., 1913, p. 31.
2. Ibid., p. 48.
3. Ibid.
4. Ibid., pp. 41, 50, 55, 62, 86; and Arnold Philip, *Journ. Inst. Met.*, xii., 1914, p. 133.

An excellent summary of the work of previous investigators is contained in Dr. Bengough's First Report to the Corrosion Committee, *Journ. Inst. Mets.*, 1911, vol. v.

DISCUSSION.

The subject of the Corrosion of the Non-Ferrous Metals was then thrown open for general discussion, and the **President** called upon Professor H. C. H. Carpenter, to open the Discussion.

Professor H. C. H. Carpenter said he thought Mr. Arnold Philip's hypothesis was untenable. The paper stated: "Both the α and β phases of brass consist of solutions of zinc in copper, and no evidence of any chemical combination between the two elements is known to exist. The surface of such brass may therefore reasonably be considered to consist of surfaces of zinc and copper in close contact." Mr. Philip had referred in his remarks to his (Professor Carpenter's) recent work on the nature of the beta constituent, and he wished to make it clear in what he was going to say that it did not depend on the acceptance or otherwise of the conclusions he had drawn from that work. He confessed that he rubbed his eyes when he read the above sentence as to the absence of any evidence indicating chemical combination between zinc and copper, because it was clearly wrong. The existence of the compound Cu_2Zn_3 was well established. There was also evidence that CuZn, and perhaps $CuZn_2$ and $CuZn_6$ existed. Mr. Philip's view might be tenable if the liquidus of the system consisted of one branch and if a continuous series of solid solutions of copper and zinc existed from one side of the diagram to the other. The liquidus, however, had no less than six branches and six solid phases, α, β, γ, δ, ε, and η, separated respectively from them. What was the reason for the separation of those phases? Tammann held the view that every solid phase had as its basis an intermetallic compound. Although this hypothesis was not universally accepted it commanded a considerable measure of assent and was at any rate plausible. It appeared to him (Professor Carpenter) that it was highly improbable in view of the above facts that condenser metal, 70/30 brass, consisted of particles of copper and zinc in close contact. It seemed much

more probable that the nature of this alloy was determined by the character of the phase fields bounding it. On one side was pure copper and on the other either β^1 or $\alpha + \gamma$. If it was β', the possible compound CuZn had to be considered; if it was $\alpha + \gamma$, then Cu_2Zn_3, corresponding to pure γ, had to be taken into account. In his view it was more probably one or other of these compounds rather than zinc which existed in 70/30 brass.

It appeared that Mr. Gibbs had come to a different conclusion from Mr. Philip in regard to condenser tube metal. He said (page 265): "A general consideration of the foregoing facts conveys the impression that a solid solution of zinc and copper is intermediate in character between a physical mixture and a chemical compound. . . . It is as though there were some kind of weak chemical combination (or rather physical combination, since the chemical character of the constituents is not changed entirely but only modified) between the two, whereby the available energy of each is diminished. . . . Is it possible that a compound or compounds of copper exist stable only at low temperatures—say below 50° C.?" He (Professor Carpenter) thought there was more to be said for this view than Mr. Philip's, but was disposed to assign more weight to possible chemical combinations between copper and zinc in this alloy than Mr. Gibbs did.

Professor A. K. Huntington supported Dr. Carpenter's view.

Dr. W. Rosenhain, F.R.S., said he was inclined to agree both with Professor Carpenter and Mr. Philip. The whole of the difficulty turned upon the conception of what an intermetallic compound was. If we could imagine that an intermetallic compound was a crystal built up of molecules, then Professor Carpenter's view was the one he should adhere to, but Bragg's recent work had completely altered the aspect of matters. It had yet to be proved that such a thing as an atomic couple could exist or could raise a current at all. The theoretical conception was possible as far as it went, but he was afraid it did not go very far, and he was inclined to doubt whether currents could be set up in that way at all. It sounded a little unlikely on the face of it; but we did not know definitely what the nature of an intermetallic compound was.

Lieutenant Ulick R. Evans (*communicated*): Mr. Philip's paper is extremely interesting, but it is impossible to regard the corrosion of brass as being due to zinc-copper couples; if brass were a mosaic of zinc and copper, corrosion would take place far more rapidly than is the case. Such a mosaic should be corroded by salt water in the absence of oxygen; for a zinc and copper plate immersed in salt solution and joined by an external wire furnishes a lasting current, I believe (the zinc dissolving and hydrogen bubbles appearing on the copper), assuming that the zinc is kept free from basic salts by scraping. But Mr. Philip himself states that dissolved oxygen is needed for the corrosion of brass.

If Mr. Philip's hypothesis were tenable, then a Daniell cell in which the zinc has been covered with black copper (by immersion in copper sulphate) should behave similarly to one in which the zinc rod is replaced by a similar rod of brass. This is not the case. The first cell provides an e.m.f. similar to that of any other Daniell cell (about 1·08 volt), while the brass cell gives a far smaller e.m.f., and polarizes far more rapidly when made to furnish a large current.

The same truth is expressed by the numbers for single electrode potentials given in Mr. W. Gibbs's paper:—

At 16° C.—	Zinc | sea-water	= −0·5100 volt.
	Brass | sea-water	= +0·3460 volt.
	Copper | sea-water	= +0·3896 volt.

Now, in the case of an alloy consisting simply of a mosaic of the two component metals, the p.d. should—roughly speaking—be that of the more electropositive metal. Where, however, solid solution is possible, the presence of even a small amount of less electropositive metal materially alters the p.d. of the more electropositive metal; this has been proved by the measurements of various observers, described in the *Zeitschrift für Physikalische Chemie* and elsewhere (not having access to these journals at present, I cannot give references). Obviously brass behaves as a solid solution, or mosaic of solid solutions, not as a simple zinc-copper mosaic; and this of course would be expected as the result of metallographic considerations.

But Mr. Philip ascribes the fact that the p.d. of brass is different from that of zinc to local currents set up, in brass, between the zinc and copper elements. This view would be tenable but for the fact that—according to Mr. Philip—such currents do not take place in the absence of oxygen. In practice, however, I think there is little difference between the p.d.'s of pure zinc and of "copper-blackened" zinc, immersed in the same solution.

Again, I cannot agree with Mr. Philip when he says that "no evidence of any chemical combination between the two elements is known to exist." The equilibrium diagram seems to me to contain ample evidence of such combination. Certainly it shows—since there are no maxima in the freezing-point curve—that the pure compounds are metastable, but undoubtedly the solid solutions which we know are not solids of zinc in copper or copper in zinc, but are solutions of a metal in a compound, or of a compound in a metal, or of one compound in another.

The hypothesis of "zinc-copper couples" has apparently been introduced to account for the fact that the "corrosion-residue consists of (*a*) unaltered brass, (*b*) pure metallic copper." The presence of pure copper in the residue does seem to need explanation. But is this copper really a "corrosion-residue"? Is it not possible that the copper of the more electropositive grains passes—with the zinc—into solution, and that the copper is then redeposited, as metal, on the less electropositive portions, the whole system becoming a minute Daniell cell? Perhaps Dr. Desch, who has studied these residues under the microscope, could tell us if this view can be maintained.

Dr. Desch in his Paper refers to the fact that the measurements of anodic corrosion (with an applied e.m.f.) of a metal have little to do with the rate of corrosion on simple immersion, without applied e.m.f.

From the standpoint of the electrochemical theory of corrosion this is quite to be expected. According to this theory, the corrosion occurring on simple immersion depends on the e.m.f. set up between dissimilar parts of the surface; thus heterogeneous materials dissolve more quickly than homogeneous ones. But, if an external e.m.f. is applied, it matters little whether the material is homogeneous or heterogeneous; pure zinc, attacked anodically, dissolves as freely as zinc containing lead particles.

The experiments of Desch and Whyte on the anodic corrosion of brass are sometimes interpreted quite wrongly, because there are some who consider that the acceptance of the "electrochemical theory" implies that the "electrochemical test of corrosion" (i.e. the anodic test) is a true criterion of corrosion during simple immersion. I am sure that Dr. Desch would be the first to oppose such an interpretation of his work.

Mr. W. E. Gibbs: I find it difficult to accept the copper-zinc-couple hypothesis of the corrosion of brass, in spite of the very able case which has been made out for it by Mr. Arnold Philip. It is at least questionable whether the individual particles of zinc and copper which are present in a

piece of brass are sufficiently large to form zinc-copper couples when the brass is immersed in a salt solution such as sea-water. If we assume that the texture of the alloy, so to speak, is so coarse that such couples can exist, then we should expect the process of the corrosion of the alloy to resemble that of a zinc-copper couple under similar conditions. When zinc and copper are electrically connected and immersed in sea-water at the ordinary temperature it is found—

(*a*) That the zinc dissolves very much more rapidly than when it is not connected with copper.

(*b*) That the copper does not dissolve at all, but becomes coated with a thin film of $CaCO_3$, precisely as a brass tube becomes coated with $CaCO_3$ when it is protected by a block of zinc in a condenser.

(*c*) That the electrode potential of the couple is that of zinc.

In other words, a zinc-copper couple when immersed in sea-water is dezincified from the very commencement of the action.

Now what is the behaviour of 70/30 brass in sea-water at the same temperature?

(*a*) The zinc in it dissolves less rapidly than pure zinc of the same concentration.

(*b*) The copper dissolves just as fast as the zinc until it becomes covered with a film of copper oxide. (Is it altogether likely that a copper cathode would become oxidized at the ordinary temperature in a cell whose e.m.f. is 0·9 volts?)

(*c*) The electrode potential of 70/30 brass resembles that of copper rather than that of zinc, and this whether the sea-water is stationary or moving.

Dezincification is only produced under special circumstances which are chemically more favourable to the solution of zinc than to the solution of copper, e.g. diminishing the concentration of salt in the sea-water, increasing the concentration of CO_2, or by applying a small e.m.f. to the brass, tending to drive it into solution.

Dezincification, therefore, is not a normal product of the sea-water corrosion of 70/30 brass. On the other hand, dezincification is the normal product of the sea-water corrosion of a zinc-copper couple. If, therefore, such zinc-copper couples do exist in brass, their behaviour is very much modified. It is difficult to see why it should be altogether different. Possibly they do not exist at all.

When two liquid metals are mixed thoroughly and then cooled quickly the resulting alloy will be one of three things. It will be—

(*a*) A solid emulsion, if the two metals are not completely miscible under the conditions (particularly of temperature and pressure) of the experiment. The character of the alloy will be that of a physical mixture. Its properties will be additive functions of those of its components.

(*b*) A solid solution, if the metals are completely miscible under the conditions of the experiment. The properties of the alloy will no longer be additive. At the same time they will still resemble those of the component metals. This is particularly true of the chemical properties.

(*c*) A solid compound, if the metals can combine chemically under the conditions of the experiment. In this case the properties of the alloy are quite different from the properties of the component metals.

The fundamental distinction between (*a*) and (*b*) appears to lie in the degree of intimacy of contact between the atoms of the component metals. This is clearly related to the state of division in which the metals are present in the mixture. The smaller the individual particles of the component metals, the greater the number of atoms of each which will be in contact with atoms

of the other. Consequently the greater will be the effect which the two metals will exert upon one another.

Is it possible that the smallest particle of a metal which can retain its physical identity unimpaired is the *crystal*, and that the limiting condition for the existence of a solid emulsion is an intimate mixture of minute crystals of the component metals? Each minute crystal would contain atoms of one or the other metal, but not both.

In a solid solution the mixture may be more intimate—in fact, intracrystalline—and each minute crystal contain atoms of both metals.

It is conceivable that in such an intracrystalline mixture the spatial proximity of the atoms of the different metals would cause them to exert a restraining or intensifying influence upon each other. At the same time they would not necessarily be chemically combined, and therefore their identity would not be entirely changed, but only modified.

The next stage in the mutual approach of the two metals would be a definite act of chemical combination between the atoms of the different metals inside the crystals.

These three types of metallic mixture may be summed up as follows :—

(*a*) An intercrystalline mixture, each crystal containing atoms of one component only. Such a mixture would possess the properties of a physical mixture.

(*b*) An interatomic mixture (intracrystalline), in which the physical properties of each crystal of a component metal are modified by the presence in it of atoms of the other component. Such a mixture is known as a solid solution. It might conveniently be called an atomic mixture.

(*c*) An interatomic combination, i.e. a definite chemical combination of the atoms of the different metals to produce a chemically distinct substance.

Intermetallic couples would probably exist in a physical mixture such as (*a*). They might exist between crystals of different composition, if such existed, in (*b*). The facts of the behaviour of alloys of the type (*b*) when corroding in sea-water do not suggest that intermetallic couples exist in alloys of the type (*b*).

I think the galvanic couple hypothesis may be applied to the corrosion of a solid solution (i.e. an atomic mixture) if we regard the couples as being intercrystalline rather than intermetallic. It would seem, for instance, that couples may exist between the α and β crystals in Muntz metal, for it is well known that the dezincification of this alloy is confined to the β phase.

In addition to couples between single crystals there may be couples set up between comparatively large areas of the surface of a solid solution owing to the existence of physical or chemical differences in the alloy itself not confined to single crystals. The corrosion of hard-drawn α solid solutions makes it seem probable that something of the kind exists. In general, such couples would be produced by any circumstance, physical or chemical, which produces differences in the solution tension of the alloy at different points of the surface. Among such external circumstances are local differences of temperature, local variations in the concentration of the sea-water, and the deposition of catalytic salts on the metal surface. Such circumstances are a common source of pitting.

Mr. Arnold Philip, *in reply*, said that he had not claimed that the zinc-copper couple hypothesis of brass corrosion was demonstrated by the facts he put forward, but it appeared to him that some hypothesis of this nature should be considered, namely, that the action of intermolecular or even interatomic couples was the cause of corrosion. It was generally agreed that corrosion was caused by metallic couples of some sort or other and the

action of metallic couples of different phases or of differently oriented neighbouring crystals of the same phase did not appear to fully account for the observed facts of brass corrosion.

The time available for discussion that night was very short, and he proposed to defer his reply until he had considered any written criticisms which might be made, but he thought that he might claim that although Professor Carpenter's views were, if correct, fatal to the possibility of the action of molecular zinc-copper couples being the cause of brass corrosion, they did not negative the possibility of molecular couples of copper and copper-zinc compounds acting in this way, whilst Dr. Rosenhain's criticism rendered it possible that zinc-copper couples of atomic dimensions might function.

(*Communicated, February* 4, 1916.)

1. The author wrote that he was aware that Professor Carpenter had in the past repeatedly stated that it was not conceivable that the α and β phases of brass could contain any molecules of zinc as such, although, on the other hand, Shepherd in his investigations on copper-zinc alloys in 1904, maintained that these all consisted of solid solutions of copper in zinc or zinc in copper.

2. If it was admitted that the chemical compound Cu_2Zn_3 had a real existence (and this was the only zinc-copper compound for which an undoubted existence was claimed by Desch), then it was not necessary to postulate the existence of any of the other more doubtful copper-zinc compounds referred to by Professor Carpenter as possibly being present in solid brass in order to maintain that the α and β phases could contain no zinc as such, provided always that the compound Cu_2Zn_3 in the liquid phase could not split up on the addition of further amounts of copper into, say, the compound CuZn and Zn or into Cu and Zn. The most convincing method of maintaining this view was, he (the author) felt, to consider what happened when successive amounts of copper were dissolved in zinc. When the amount dissolved rose to 39·26 per cent. by weight, which corresponded with the percentage composition of the Cu_2Zn_3 compound, then, provided that this alloy in the liquid phase consisted of nothing except molecules of Cu_2Zn_3 and provided no splitting up of Cu_2Zn_3 could take place, further amounts of copper dissolved in this could give only solutions of copper in Cu_2Zn_3 or of Cu_2Zn_3 in copper, and hence the α and β phases could contain no free zinc if on cooling from the liquid no splitting up took place.

3. If this view was correct, then it was clear that the zinc-copper-couple hypothesis necessitating molecular couples of zinc and copper must be untenable, although corrosion caused by Cu and Cu_2Zn_3 molecular couples was not negatived and the modified form of atomic zinc-copper couples suggested as being possible by Dr. Rosenhain was also conceivable.

4. But had Professor Carpenter supported such a view as he (the author) had set out in paragraph 2 above? As far as he (the author) could understand, he had not, but he had adopted what appeared to be a somewhat inconsistent position.

5. Professor Carpenter believed that the copper-zinc compound CuZn (49·2 per cent. Cu) existed, but he also believed that brass alloys containing only the α constituent were to be regarded as apparently homogeneous mixtures of very minute crystals of copper and β, which at ordinary temperatures changed slowly into a mixture of minute crystals of copper, and γ.* Dr.

* Carpenter and Edwards, "A New Critical Point in Copper-Zinc Alloys," *Journal of the Institute of Metals*, No. 1, 1911, vol. v., pp. 147–9.

Rosenhain had criticized this view in so far as it referred to the possibility of these different phases existing as crystals, by remarking that "the view that a solid solution was a homogeneous mixture of the crystals of the two metals or intermetallic compounds was to his mind incompatible with the phase rule." * The precise nature of the units in which the copper and the γ constituent existed, *i.e.* whether they were molecules, as these entities were ordinarily understood to exist by chemists, or whether they were minute crystals as stated by Professor Carpenter, might, however, for the sake of clearness be now left out of consideration.

6. Under these conditions Professor Carpenter's claim amounted to this, viz. that α brass, when properly cooled for a sufficiently prolonged period, consisted of an intimate mixture of some kind of chemical or physical units of copper and of γ, with possibly some other zinc-copper compound or compounds.

If by γ Professor Carpenter referred to the whole γ *phase* of brass, then this, as he (the author) understood it, might contain zinc units towards the zinc end of the phase field, and if so, Professor Carpenter must admit that α-phase brass might contain zinc; but if by γ Professor Carpenter meant the chemical compound Cu_2Zn_3 which occurred possibly pure at the copper end of the γ phase and was therefore possibly a special form of the γ phase which could not contain any zinc units, then he was assuming that a compound Cu_2Zn_3 containing 39·2 per cent. of copper and which therefore, in the equilibrium diagram, was well to the zinc side of the compound CuZn (49·2 per cent. Cu), had passed into α-phase brass.

7. Professor Carpenter's view, therefore, appeared to be that it was permissible to explain the mechanical brittleness of 70/30 α-phase brass at 470° C. by assuming that units of a compound Cu_2Zn_3 existed in it as such although an intermediate compound CuZn came between the α-phase material and the Cu_2Zn_3 compound, but yet at the same time that it was not permissible to attempt to explain peculiarities in the phenomena of the corrosion of α and β-phase brasses as the author had done by assuming that they contained units of zinc as such, on account of the fact that intermetallic chemical compounds of copper and zinc existed in the β and γ phases which intervened on the equilibrium diagram between α-phase brass and zinc.

8. In other words, the compounds CuZn might be split up on additions of further amounts of copper into the two units—copper on its copper side in the equilibrium diagram and Cu_2Zn_3 on its zinc side, but it was not possible to admit that the compound Cu_2Zn_3 could be similarly split up into the units CuZn on its copper side on the diagram and Zn on its zinc side. What experimental facts could Professor Carpenter bring forward to justify this view of the possibility or otherwise of the splitting up of intermetallic compounds?

9. The nature of intermetallic chemical compounds and the precise composition of the molecular entities in intermetallic mixtures was in fact at present an obscure matter for several reasons. The stoichiometric relations between the elements of such compounds and their method of splitting up or dissociation in liquid and in solid solution appeared to differ markedly from those of other chemical compounds in liquid solutions, and he did not consider that the absence of zinc molecules *qua* zinc in the α and β phases of brass could be regarded as established.

10. As far as the statement which the author had made in his Paper that both the α and β phases of brass consisted of solutions of zinc as zinc in

* *Journal of the Institute of Metals*, No. 1, 1911, vol. v., p. 159.

copper was concerned, he had not meant to claim that there was no evidence that the compound Cu_2Zn_3 existed in the γ phase, and in reading his Paper he had implied that this was so by an introductory remark, which now appeared as a footnote, in which he referred to the view which Carpenter and Edwards had originated, namely, that the β^1 phase actually consisted of a mixture of finely divided α and γ. The view which he had put forward was, that neither the presence of the compound Cu_2Zn_3 nor of any other copper-zinc compound had ever been detected, as far as he was aware, as such by chemical or microscopical or other direct observations in either the α or β phases of brass.

11. He, however, considered that where he had made the statement in his paper that there was no evidence of any chemical combination between the copper and zinc in the α and β phases of brass, he had certainly overstated his case, and that he should alter the words (*supra*, p. 244) from "*no evidence*" to "*no direct evidence*," a correction which had been made in the paper as it now appeared; whilst on p. 257 he had altered the words "as zinc and copper are not in a state of chemical combination in either the α or the β phase" to "as zinc and copper are not *necessarily* in a state of chemical combination," etc.

12. It was, he thought, a generally accepted view that the corrosion of brass immersed in an electrolyte, besides being due to differing strain conditions or temperature conditions of the surface, also took place by the functioning of some kind of metallic couples located on the surface of the brass.

13. As he had stated in his Paper, he had not been able to satisfy himself that the hypothesis that these intermetallic couples were of molecular zinc and copper was either true or untrue, but this hypothesis appeared to explain some facts which were not explained by considering that the corrosion was due to the action of the larger couples formed of different phases of the copper zinc alloys or of neighbouring crystals of a single phase which possessed different orientations.

14. If only molecules of Cu and of Cu_xZn_y were present in α and β brass, as Professor Carpenter held, the possibility of the action of such $Cu/Cu_xZn_y/$couples must be considered; or if molecules of Cu, Cu_xZn_y, and Zn were present, the action of molecular couples or any of the molecules present might function; whilst Dr. Rosenhain's remarks suggested the possibility not of molecular but of atomic couples being considered electrolytically active.

15. If he understood Dr. Rosenhain's criticism correctly, it was to the effect that if any single-phase alloy of brass consisted of a solution of copper-zinc compounds such as, say, Cu_2Zn_3 dissolved in copper, the surface of such an alloy could not corrode, due to the action of surface couples formed of molecules of Cu_2Zn_3 and of copper of the dimensions hitherto conceived to be molecular, but that if corrosion could be caused by couples of that order of dimensions, they must consist of atoms and not molecules of copper and zinc.

16. In fact, he gathered that Bragg's researches on the nature of the molecule in crystalline solids ruled out the possibility of a molecule, in the hitherto accepted meaning of that word, acting as a unit in a molecular couple, and that the nearest approach to such a conception either when dealing with a solution of zinc in copper or of any copper-zinc compound, say Cu_2Zn_3 in copper, must be atomic couples of zinc and copper. If this was so, such atomic zinc-copper couples could equally well function (if they functioned at all) in any conceivable alloy of copper and zinc, whether this alloy consisted of a solution of zinc in copper or of any copper-zinc compound dissolved in

either copper or in zinc. That is to say, unless it could be shown that atomic couples could not function, Bragg's results appeared to indicate that any small corrosion elements on the surface of well-annealed single-phase brass if not due to the different orientation of contiguous crystal areas, must be due to atomic couples of the form Zn/Cu and not of the molecular form Cu_xZn_y/Cu.

17. The author did not consider that it was necessary that the corrosion of brass if caused by zinc-copper couples, whether molecular or atomic, would involve such high corrosion velocity as Mr. Evans suggested ; the neighbouring areas of copper and zinc would be very minute and very close to each other, polarisation would rapidly set in, and the nature of the electrolyte at the surfaces would quickly alter.

18. It had not been his (the author's) experience that a zinc and copper plate immersed in a salt solution and joined by an external wire would furnish a lasting current in the absence of oxygen ; in fact, after completing such a circuit he considered the current originally produced would very rapidly fall to what was known as the residual current, due to the diffusion of the products of the electrolysis from the electrodes. Dissolved oxygen or some other depolariser was required for the corrosion of brass in salt water, and was also necessary for causing the solution of the zinc of a pair of zinc and copper plates immersed as described by Mr. Evans.

19. Mr. Evans's objection that mechanical mixtures of copper and zinc did not give the same electrode potentials to sea-water as a corresponding brass was a more serious objection, but the author had alluded to this point in his Paper, and had suggested an explanation which, where the areas of the couples were reduced to minute dimensions, might account for the fact that a brass surface, if made up of contiguous copper and zinc areas, might possess a markedly higher electrode potential than that of zinc.

20. Mr. Evans had remarked that the hypothesis of zinc-copper couples had apparently been introduced to account for the fact that the corrosion residue consisted of (*a*) unaltered brass and (*b*) pure metallic copper. This was true, but it was also proposed as accounting for the facts observed by Bengough and Jones that Muntz's Metal corroded more slowly than 70/30 brass under the same conditions as to corroding liquid temperature, etc.,* and for the facts of electrolytic corrosion as observed by Desch and Whyte.

21. The most serious objection to the possibility of a zinc-copper couple being the cause of the corrosion of brass was, in the author's opinion, that which was raised by Mr. Gibbs, who stated that when 70/30 brass was immersed in sea-water the copper dissolved just as fast as the zinc until it became covered with a film of copper oxide. This fact concerning the corrosion of brass was, he believed, quite novel, and, as far as he saw, if substantiated rendered the hypothesis of the zinc-copper couple corrosion of brass untenable, although molecular couples of the form Cu_xZn_y/Cu were still possible. It was, however, remarked that he understood Dr. Desch considered that dezincification always took place as a first stage in the corrosion of brass, and if Dr. Desch's views on this point were correct they appeared to be in contradiction to the claim which Mr. Gibbs made that copper dissolved as readily as zinc in the initial stages of corrosion. It would therefore be necessary to await further evidence, which he understood Mr. Gibbs would shortly publish, upon this point.

22. The suggestion which Mr. Evans made that in the corrosion of brass the copper of the more electropositive grains passed, with the zinc, into solution

* Bengough and Jones, "Second Report to the Corrosion Committee," *Journal of the Institute of Metals*, No. 2, 1913, vol. x., p. 32.

and that the copper was then redeposited as metal on the less electropositive portions was of interest. It was a similar action to that alluded to by Dr. Desch in his paper on "Physical and Mechanical Factors in Corrosion" * as explaining the curious behaviour of pure lead foil immersed in a slightly acid solution of lead nitrate or acetate. It might also explain the fact which Dr. Desch had observed, that dezincification always appeared as the first stage of brass corrosion; whilst it might further, perhaps, explain in some way the fact observed by Mr. Gibbs, that in the first stage of brass corrosion the copper dissolved as rapidly as the zinc.

23. In conclusion, the author begged to thank those who had kindly taken part in the discussion of his Paper for their very interesting criticisms. The object of the Paper was to call attention to the possibility of molecular couples, possibly of zinc and copper but also possibly of molecular couples of compounds of zinc and copper, as offering an explanation of some aspects of brass corrosion which was not completely given by the hypothesis that corrosion was caused by couples formed by contiguous portions of different phases or contiguous crystals of a single phase but possessing different crystalline orientation. He felt that the question still remained an open one.

Dr. Cecil H. Desch wrote (*reply communicated February 27, 1916*) that the discussion had been a fruitful one, and that several points had been brought into prominence. He was convinced that the factors to which he had alluded in his own contribution must receive consideration, and that all views of corrosion which only took electrolytic potential and solution pressure into account were incomplete, as changes of texture, etc., were capable of altering the circumstances to such an extent as even to reverse the order of the changes which might theoretically be expected.

He was still of the opinion, maintained by Mr. Whyte and himself, that the corrosion of brass and yellow metal was in all cases initially one of dezincification, and that the formation of copper oxide was always a secondary effect due to the action of oxygen on the very finely divided and chemically active copper left as a residue from the brass. He could not agree with Mr. Gibbs that copper and zinc dissolved together until the metal was protected by copper oxide. The amount of copper dissolved in the primary process was exceedingly small, but after the secondary changes had set in a much larger quantity might be dissolved, this depending on the external conditions. Mr. Evans's suggestion that the copper was dissolved and redeposited was interesting, but he had seen nothing in the course of his microscopical investigations to support such a view. Were it so, one would expect the copper to be deposited on the nearest compact surface, but actually it always occupied the exact position of the alpha or beta solid solution from which it had been formed by dezincification. So completely was this the case that a section of corroded yellow metal bolt was often indistinguishable in a photograph from one which had been prepared by etching a piece of the fresh metal, although in the former specimen the metal was a mere pseudomorph, the constituents being completely replaced by spongy copper, retaining the form of the original alloy. This was well seen in Figs. 6 and 7 of Mr. Whyte's paper. †

With regard to the question of compounds of copper and zinc, he agreed with Professor Carpenter that one must assume the existence of several such compounds, and in his *Intermetallic Compounds* ‡ he had given the existence of CuZn and Cu_2Zn_3 as certain, and that of $CuZn_2$ and a fourth compound, possibly $CuZn_6$, as probable. This conclusion was reached from a considera-

* *Supra*, p. 198. † *J. Inst. Metals*, 1915, **13**, p. 88, Pl. II.

‡ London, 1914.

tion of the electrical conductivity and its variation with temperature, but he also thought that the view suggested by Professor Carpenter, that every intermediate solid phase contained a compound, had much to support it.

He could not help thinking that the consequences of Bragg's most important results in regard to the structure of crystals were occasionally pressed too far in these discussions. Professor Bragg's results did not justify the view that the conception of the molecule had no meaning in the solid state, although they undoubtedly showed that the space-lattice was essentially an atomic structure. If, however, one considered the colour of the alloys of copper and antimony, for instance, it seemed that in the violet compound Cu_3Sb the grouping of the atoms of the two metals must be such that the characteristic properties of the components had been destroyed and replaced by others. This space-lattice was probably a complex one, but it would be possible for the atoms to be associated in such a way that the grouping Cu_3Sb retained its individuality throughout. The discussion of this point would occupy too much space, and would be somewhat outside the scope of the present discussion. There was also the evidence of electrical conductivity and hardness. Where an intermetallic compound occurred in the middle of a series of solid solutions, as in the alloys of magnesium and cadmium or of antimony and tellurium, these properties, and others allied to them, such as the thermoelectric power, changed discontinuously, which could hardly be the case if there were no difference between a space-lattice composed of free atoms and one in which the atoms were united to form a definite compound.

DEMONSTRATION OF THE CUMBERLAND ELECTROLYTIC PROCESS FOR PREVENTING CORROSION OF ALL METALS IMMERSED IN LIQUIDS.

At the conclusion of the Discussion **Mr. Elliott Cumberland, M.I.M.**, gave a Demonstration of his Electrolytic Process for Preventing Corrosion of all Metals Immersed in Liquids.

While some investigators have been studying the question of producing a non-corrodible metal, others have given their attention to solving the problem of effectively protecting all metals from corrosion.

The Committee appointed by the Institute of Metals in the early part of 1910 to investigate the causes of corrosion of non-ferrous metals and alloys has brought forward a large amount of valuable data and information on this subject.

Mr. S. Whyte, in his Paper dealing with the microchemistry of corrosion,* gives some very conclusive proofs that the nature of corrosion of these alloys is in all cases primarily dezincification, and points out that when, in his experiments, corrosion was hastened by an applied electromotive force, the nature of the action was similar to that found in actual service conditions.

Sometimes we have conflicting evidence, but in these cases the evidence which comes from actual working conditions must be taken in preference to the experimental facts brought to light in the laboratory.

Dr. G. D. Bengough and Mr. Arnold Philip differ considerably over the question of the effect of carbonaceous matter in contact with the water-side of condenser tubes, and I think Mr. Philip's views meet with the approval of the majority. Practical experience has shown that such an electro-negative substance as carbon in contact with brass condenser tubes very often causes and accelerates corrosion.

Professor Ernst Cohen of Amsterdam, in his Paper on "The Corrosion of Condenser Tubes and Sea-water Conductors," read before the Institute of Naval Architects, 1902, makes some very interesting remarks on the use of iron and zinc for protecting condenser tubes from corrosion. He says: "If the zinc is in good metallic contact with the tubes they will not corrode, but if the resistance between the two metals becomes too great, the protective action disappears. This seems to point to the fact that the intensity of the electric current in the system is playing a part. By increasing the intensity of the electric current by means of an auxiliary battery, the protective action of the zinc is re-established." In another part of his Paper he points out that "direct electric current produced by leakages, though only very

* Part III, "The α, β Alloys of Copper and Zinc."

small, may give rise to corrosion." "This phenomenon will only be produced by this cause when the condenser tube is connected to the positive pole of the dynamo."

It is recognized generally that corrosion of all metals is due to galvanic electrochemical action, and many and varied are the protective methods adopted. Metal structures have been painted, zinc and tin coatings in the form of galvanizing have been applied with some measure of success; but it has been found that these become cracked and removed in patches, and the exposed portions of the structure then deteriorate more rapidly.

Iron and steel, it is well known, contain other elements, the presence of which imparts special properties fitting the iron or steel for specific purposes. It is the action of these incorporated elements, in conjunction with the surrounding fluid, which often causes the trouble. Galvanic cells are formed, and the electro-negative particle is always protected at the expense of the electro-positive particle.

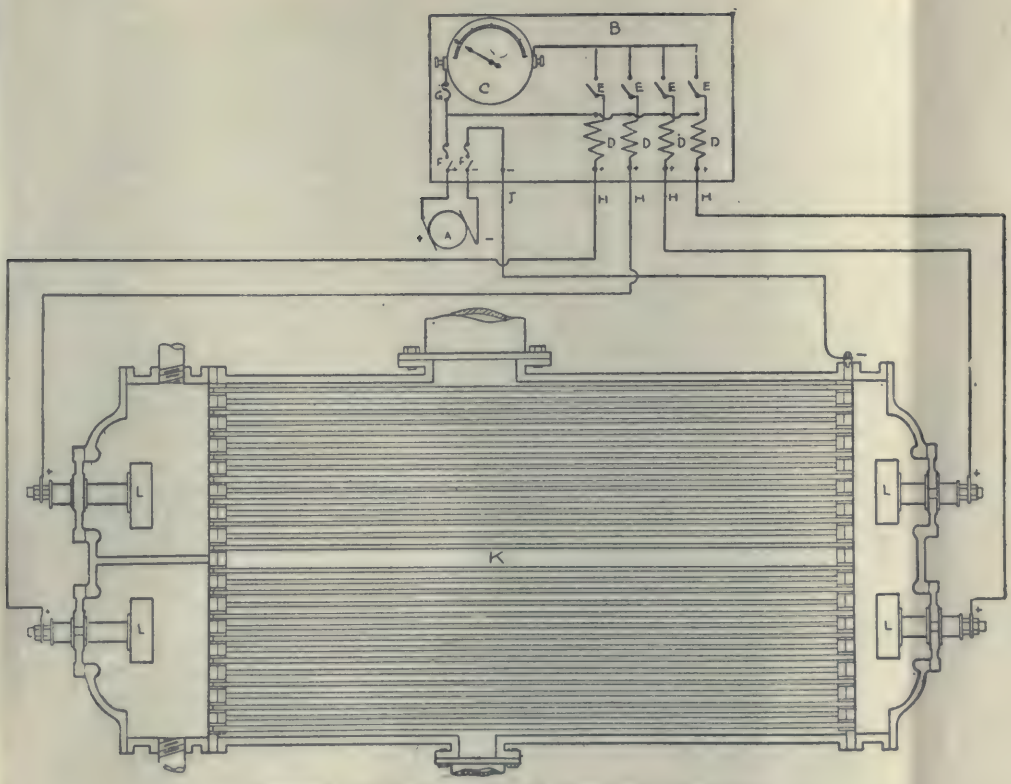
Thermo-electric couples also exist, due to variations in temperature. Evidence of this is found on the water side of the furnaces in boilers along the line of fire-bars, and much of the deterioration of hot-water pipes is due to electrolytic action between the hot and cold portions.

Galvanic action also occurs between the harder and softer portions of a commercially pure metal. This is met with in parts of boilers which have been flanged, riveted, and caulked, and is noticeable in the case of copper pipes, especially where they form bends and have been subjected to hammering in the course of manufacture. This deterioration of copper pipes is remarkably rapid, and may take the form of pitting over certain areas or show up as grooving, according to the manner in which the metal has been strained.

Fire mains in warships suffer in this way, and efforts have been made to overcome the trouble in these by fitting short lengths of cast-iron pipes at intervals which can easily be renewed. The cast iron, being electro-positive to the copper, transfers the corrosive action to itself. The drawback to this method is that it is only temporary, while the cast iron is new and clean, and reversal of polarity soon occurs, due to the oxides and products of corrosion being electro-negative to the copper.

The injection and discharge pipes used for circulating sea-water through the main condensers suffer considerably from this form of corrosion—especially in the case of battleships and large mail steamers fitted with turbine propelling machinery, because the connections between the condenser and the turbine are large and rigid, and to allow free expansion of the turbine casing the condenser is fitted with sliding feet; therefore, where the inlet and discharge pipes are comparatively short in length, strains are set up, and the result is severe corrosive action. In consequence, copper has been discarded for this purpose in battleships, and cast brass pipes of much greater thickness than the copper have been adopted to ensure a longer life. These are very expensive and difficult to manufacture, but the chief disadvantage is that they are rigid and more liable to fracture than the ductile copper pipe. Obviously the better course would be to retain the copper pipe and protect it from this corrosive action.

Let us consider the surface of an alloy containing segregated portions of its different component metals. These parts have differences of electrical potential in proportion to the position of the component metals on the galvanic potential scale. When the liquid forms the conductor or electrolyte, the flow of electrical energy is from the high potential to the low, and the metal from which the current enters the liquid suffers electrochemical change in



CUMBERLAND INSTALLATION IN SURFACE CONDENSER.

FIG. 1.—A—Motor Generator ; B—Switchboard ; C—Ampmeter ; D—Adjustable resistance coils ; E—Two-way switches ; FG—Fuses ; H—Wires from positive pole to electrodes ; J—Wire from condenser shell to negative pole ; K—Condenser ; L—Insulated bolts and electrodes.

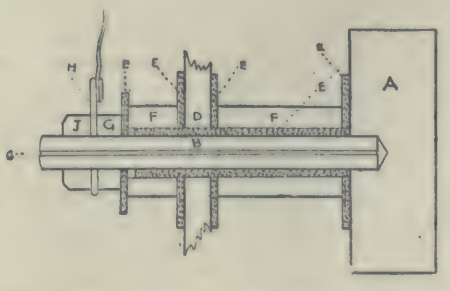


FIG. 2.—A—Electrode ; B—Insulated support ; C—Tell-tale bore ; D—Condenser shell ; EF—Insulation ; G—Washer ; H—Lug connection to wire from positive pole ; J—Nut.

the form of corrosion. The reason corrosive action is more pronounced when metals are in contact with sea-water is because this forms a better electrolyte.

Quite apart from the considerable costs of effecting repairs to condensers, and the inconvenience caused, it is of great importance that salt water should not enter the boilers by way of the contaminated feed due to leaky tubes. If this occurs, any corrosive action which is present in the boilers is greatly accelerated. Care must also be taken that no particles of brass, copper, graphite, zinc oxide, or other electro-negative metals are allowed to enter boilers, as they have the effect of producing severe corrosive action when in contact with the steel plates of the boiler, and this is increased by the perfection of their contact with the steel.

The idea that appeals to many is to succeed where the promoters of alloys fail, and discover a perfectly non-corrodible metal which would withstand working stresses, etc. I contend that, apart from being almost impossible, it is not necessary, and all that is required is to render all or any metal immersed in liquids non-corrodible, and I will endeavour to show how this can be achieved.

It is recognized that galvanic action is the general cause of corrosion, and the use of electro-positive auxiliary plates dates back to the days of Sir Humphry Davy. This method is still much respected by engineers and has become popularized by long use.

If used in sufficient quantity and properly fitted, zinc and iron are effective in lessening corrosive action of structures composed of metals lower in the galvanic or electro-potential scale. H. de B. Parsons gives the amount of zinc necessary for the protection of the internal surfaces of steam boilers as 1 sq. ft. of zinc to 50 sq. ft. of heating surface. The electro-negative metal is always protected at the expense of the electro-positive ; the latter, however, changes its surface formation, due to electrochemical action, and these auxiliary plates, if not frequently changed, become electro-negative to the structure and accelerate instead of retard corrosion. The rule in the British Navy is, I believe, to renew the zincs when the decomposition has gone a quarter of an inch deep in the plates.

The scale from old zinc plates can be tested and found to be electro-negative to many metals which new zinc is capable of protecting. By means of a small tank, a milliamperemeter, and a few plates of different metals, I will later give an ocular demonstration of the futility of resorting to this kind of protection, which should be of special interest in view of the present remarkably high price of pure zinc.

My electrolytic method consists of introducing a higher counter electromotive force to that causing the corrosive action, and has achieved success in practical working conditions for many years, and has proved itself to be the only effective method of overcoming the dezincification of condenser tubes.

In this system, whereby an adequate supply of protective electromotive force can be introduced to overcome permanently all corrosive action, continuous current is supplied by an electroplating type of dynamo, working at 10 volts, to anodes consisting of pieces of iron suspended in the liquid and suitably insulated from the vessel to be protected. All corrosive action is thereby transferred from the structure to the inserted iron, and any local differences of potential in the structure itself are rendered harmless.

The structure is protected at the expense of these iron anodes, which are designed to last from eighteen months to two years. The attention required is that usually given to a small electric motor, and the cost of current is very small, owing to the low voltage used.

For many years this system has been used in all types of steamships and many large power plants on shore, and has proved successful in severe cases when other methods had failed.

I have found that the regular working of my electrolytic system has a most remarkable effect in removing hard scale from heating surfaces, etc., and preventing its further formation. From the steam-user's point of view, this is an asset of no small importance, in view of the heat-insulating properties of scale. It has been stated on good authority that $\frac{1}{10}$ of an inch of scale in steam boilers has been known to cause a loss in fuel efficiency of 10 per cent.

The advantages of this simple and inexpensive method of preventing corrosion and eliminating trouble from scale formation are obvious. The tank experiments will show clearly the effect of immersing dissimilar metals in water, and the zinc method of protection, also the reversal of polarity which ensues if zinc is not frequently renewed, and how by introducing a continuous current from an external source all metals can be rendered immune from corrosion.

The diagram shows my system fitted to a surface condenser. The insulated iron electrodes L are in all cases attached to the positive pole of the generator, and the body of the condenser is connected direct to the negative pole. All parts of the condenser in contact with the circulating water are protected at the expense of the electrodes, which are easily renewable. The amount of protective current is controlled by the adjustable resistance coils D.

In regard to the use of zinc in boilers, the naval practice is to fit 1 square foot of zinc for every 50 square feet of heating surface, and this has to be renewed after less than two months' running. It is generally fitted in slabs about 12 inches by 6 inches and 1 inch thick, and as it must always be in good metallic contact with the boiler to be effective, this entails no small amount of labour. The blue print here exhibited and provided by the Cunard Company shows the method of fitting zinc plates to the boilers of the R.M.S. *Mauretania*. There are 84 of these plates in each boiler, and these are renewed at least four times per year. Each plate is of pure rolled zinc weighing about 20 lb. At the present price of zinc this would mean about £1 per plate, or an annual cost per ship of £8,400.

The Union Steamship Company of New Zealand adopted the author's system many years ago, and it is at work in the boilers of their whole fleet. The White Star Company were among the first in this country to adopt it, and some of their leading ships have had nearly three years' experience with it. The results are so satisfactory that they are not only installing the process in their boilers and condensers, but also in the fresh and salt-water tanks. The R.M.S. *Britannic* is one of the first ships to be so installed.

The process recently has been adopted by the British Admiralty in the boilers of one of their ships.

In conclusion, I would point out that the application of this system is not confined to boilers and condensers; it may be applied with equal advantages to economizers, tanks, propellers, stern frames of ships—in fact, all metals immersed in or in contact with water or other corrosive liquids.

REVIEWS OF BOOKS.

The Molecular Volumes of Liquid Chemical Compounds. By GERVAISE LE BAS, B.Sc. (Lond.). Monographs on Inorganic and Physical Chemistry. (London, 1915: Longmans, Green & Co., Pp. xii +276. Price 7s. 6d. net.)

The author, who has published several papers on the subject, deals in a very comprehensive manner with a branch of chemistry in which painstaking investigators are gradually building up from a formidable mass of data a system of correlating the molecular volumes of organic liquids with their constitutions. It seems, however, unreasonable in the present state of our knowledge to assume that because two very reliable workers have found different values for the molecular volume of *o*-xylene at its boiling-point, this compound exists in two stereoisomeric forms, in one of which the methyl groups are situated on the same side of the benzene ring and in the other on opposite sides. For similar unjustifiable reasons the author postulates the existence of two thymols.

The writer certainly does not exaggerate in his statement in the Preface : "No physical property is apparently so well adapted to elucidate the ring structure of a compound as molecular volumes," but when he applies the theory to the terpenes he fails signally. In this section the constitutional formulæ and the names beneath them very often do not agree ; thus the name camphene occurs under the formula of bornylene ; and the arguments which follow are thereby rendered absurd. Again, the author states that in carvene (molecular volume 190·3) the hydrogen atoms in the nucleus resemble those of benzene, while in limonene (molecular volume 193·1) they resemble those of hexahydrotoluene. As is well known, however, carvene is but another name for limonene, and hopeless confusion again results. The printer, or perhaps more probably the author, since the innovation occurs consistently throughout, has invented an orthography of his own, for the following words are invariably spelt thus : olefin, quinolene, pyridene, to name but a few. The way in which the calculations are crowded into small spaces renders it extremely difficult in many cases to follow the steps by which the results are obtained, and the book's usefulness would have been considerably increased by the inclusion of an index.

The Theory of Valency. By J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Second Edition. Textbooks of Physical Chemistry. (London, 1915: Longmans, Green & Co. Pp. xiv + 192. Price 5s. net.)

The appearance of a new edition of a well-known book on a fascinating subject is very welcome. The general treatment of the subject has not been altered, but additions have been made to the extent of twelve new pages. The atomic weights have been revised throughout in accordance with the 1916 list of the Atomic Weights Committee. In a subject for which new theories are propounded almost annually one expects many changes in six years. The existence of the phenomenon of valency isomerism is now doubted, and we must believe that "there is no essential difference between principal and auxiliary valencies." It seems that in the ammine derivatives

the strength of the auxiliary valencies is a function of the atomic volume of the metal in question, one rising as the other falls. The latest views on atomic structure and the electronic theory of valency are dealt with in four closely printed pages, and J. J. Thomson's new conceptions and his symmetrical benzene formula have been included. So, too, has the latest evidence for the trivalency of carbon in certain compounds. Dr. Newton Friend has again succeeded in presenting a book which is thoroughly up to date and which all interested in Physical Chemistry will find of great use.

Organic Chemistry or Chemistry of the Carbon Compounds. By VICTOR VON RICHTER. Vol. I. Chemistry of the Aliphatic Series. Translated by PERCY E. SPIELMANN, Ph.D., B.Sc., F.I.C., A.R.C.Sc. (London, 1915: Kegan Paul, Trench, Trübner & Co., Ltd. Pp. xvi + 720. Price 21s. net.)

It is to be regretted that there is so little enterprise in this country that it needs six years to produce a translation of a work as unique in its characters as is Richter's Handbook, and since no attempts have been made to present any more than a practically literal translation, the book is sadly behindhand in very many instances, as in the case of carbohydrates. Moreover, Dr. Spielmann's task was no light one, by reason of the thousands of compounds mentioned in the volume, and it is, therefore, not surprising that reference was, in general, not made to original sources in order to verify facts. This leads to mistakes which occur in the German edition being included in the translation. For instance, we read dulcitol "is almost insoluble even in boiling water."

The work deals with a large number of compounds, giving information as to their sources and chief physical constants and chemical properties. On the other hand, very little space is devoted to general principles. This is unfortunate, since a proper understanding of such subjects as the mechanics of chemical reactions and the relation between constitutional formulæ is nowadays essential to the organic chemist. The book is thus a work of reference and not a textbook, and will certainly prove of great help to all who require a treatise of the former kind.

A great drawback is the omission of investigators' names except in rare instances. Their inclusion, however, would have caused an enormous increase in the size of the book, which, although containing over seven hundred closely printed pages, is yet a wonderful example of compression.

A start has been made, and we now have our translation. One hopes that in more favourable times a new German edition will always be followed by a translation within a year, unless in the meantime an English work of equal merit be written.

An Introduction to the Physics and Chemistry of Colloids. [Text-books of Chemical Research and Engineering.] By EMIL HATSCHEK. Second Edition, with 17 Illustrations. (London, 1916: J. & A. Churchill. Pp. 107. Price 3s. net.)

The second edition of this little text-book does not differ very widely from the original edition as issued some three years ago. No attempt at general expansion has been made, but an Appendix has been added in which a brief account is given of the devices used in the investigation of colloids and of some of the more important types of apparatus. This brief addition should enhance considerably the value of the book to those who are called upon to carry out experimental work on colloids.

Relativity and the Electron Theory. [Monographs on Physics. Edited by Sir J. J. THOMSON, O.M., F.R.S., and FRANK HORTON, Sc.D.] By E. CUNNINGHAM, M.A. (London, 1915: Longmans, Green & Co. Pp 96. Price 4s. net.)

The purpose of this book is to give students of experimental physics some idea as to the bearing which the Theory of Relativity, as developed by Einstein and Minkowski, has on what may be called the classical presentation of electromagnetic theory. The impossibility of determining by observation the absolute velocity of a body through space, which is the foundation of the principle, is obviously intimately connected with the problem of the existence of an objective æther and its relation to matter, and there is no more promising approach to this problem than through the avenue of the electron theory, which is a kind of ultimate analysis—as far as we have gone—of matter in motion. The conception of Relativity is without doubt going to modify profoundly all our existing physical notions; already Minkowski has put forward the brilliant idea of a 4-vector in which time and space are but aspects of a single underlying unity, and this, be it noted, on a physical (the conception of simultaneity of events) and not on a metaphysical basis, and it is impossible to conceive what further results may be reached when the principle has been worked out completely to its logical conclusion.

It is books like the one before us which will enable the busy student of physical science to keep alive to the possibilities of the new ideas, and it is that which gives it its chief value. The book is by no means easy reading, for extreme compression has been used and many steps in the argument are either assumed or ignored, but a wide range of application of the theory has been skilfully covered in a very small space, and those who wish for more will at once turn to the larger treatises of the author or others already existing on the subject.

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